REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS FROM OFFSHORE PRODUCED WATER BY ADVANCED OXIDATION TECHNOLOGIES

by

©Jisi Zheng

A Thesis submitted to the School of Graduate Studies

in partial fulfillment of the requirements for the

Degree of Doctor of Philosophy

Faculty of Engineering & Applied Science

Memorial University of Newfoundland

Octobor 2017

St. John's Newfoundland and Labrador Canada

Abstract

As the largest waste stream from offshore oil and gas industry, offshore produced water contains dissolved toxic organic pollutants that are hard to be removed by conventional wastewater treatment technologies. Among those pollutants, polycyclic aromatic hydrocarbons (PAHs) are of growing concern due to their high toxicity and persistence in the marine and coastal environments. Removal of PAHs from produced water before disposal is thus essential for offshore oil and gas production. However, the offshore operation and facilities (e.g., platforms and ships) usually have many special technical and economic constraints that limit the applications of many treatment technologies. Since advanced oxidation processes (AOPs) are featured with high cost-efficiency, small footprints, and eco-friendliness which well match with the requirements of offshore operation and present a promising treatment option for offshore wastewater (e.g., produced water). However, limited research efforts have been reported in investigating AOPs' mechanisms, performance and applicability in treating offshore produced water. In order to help fill the knowledge and technical gaps, this research aimed at development of advanced oxidation technologies for removal of PAHs from offshore produced water treatment and examination of the oxidation processes and kinetics, and effluent toxicity and biodegradability.

To ensure efficient, reliable, and acurate analysis results, a refined analytical method, Vortex and Shaker Assisted Liquid-liquid Microextraction (VSA-LLME), was first developed, tested and adopted in the analysis of 16 priority PAHs recommended by U.S. Environmental Protection Agency. Under the optimized condition, the enrichment factors

ranged from 68 to 78. The recoveries of the method were 74 to 85%, and the limits of detection were as low as 2 to 5 ng/L. The linearity results (R^2 values) for 16 PAHs were all above 0.99 with the relative standard deviations (RSD%) of 6 to 11%. This method also creatively utilized the organic constitutes in produced water as dispersive solvents to reduce the solvent consumption. Its straightforward procedure and excellent performance showed a strong potential for application in research and regulatory and industrial practice.

The photolysis of 16 PAHs in offshore produced water was then thoroughly investigated in this research. The results indicated much more complex kinetics in the removal of PAHs from produced water than those in stilled water, mianly due to the complex chemical constitutions of the substrate. The experiment disclosed the unique mechanisms including direct photolysis, dynamic light screening, and radical induced organic synthesis. A novel kinetic model involving dynamic light screening was developed and approved to support the mechanism analysis, and a semi-empirical model was also established to simulate the photolysis process. The proposed mechanisms and kinetics not only helped answered some scientific questions but also showed strong practical significance for further AOP development and applications.

The performance of ozonation in removing polycyclic aromatic hydrocarbons (PAHs) from offshore produced water (OPW) was studied. The experimental results showed that ozone dose had positive effect due to enhancement in ozone decomposition, and radical yield. On the other hand, the removal was suppressed at increased bubble size and pH, which may be attributed to the reduction of interfacial area as well as stronger radical scavenging effect, respectively. Microtox tests showed that the acute toxicity of OPW was reduced after ozonation, which was highly correlated with the removal of PAHs. Such

reduction was inhibited at high ozone doses, possibly due to the formation of disinfection by-products via reactions with halogens. As compared to control, ozonated OPW had higher oxygen uptake and less organic residual after biodegradation, indicating more bioavailable organics were formed after ozonation. Results from this study can be used as good references for designing new or upgrading existing OPW treatment systems using ozonation.

Based on the experimental results, the three major mechanisms affecting the PAHs removal through AOP treatment were proposed in the first time. Novel kinetic models based on the dynamic oxidant competitiveness was developed and validated. The model was able to simulate the oxidation processes, quantify the effects of different operational parameters. The testing result also indicated that insufficient treatment could lead to carcinogenetic by-products. On the other hand, proper advanced oxidation technologies could significantly increase biodegradability, showing strong potential of combining with conventional biological treatment in practice.

Acknowledgments

First and foremost, I would like to express my sincere appreciation to my advisors, Dr. Bing Chen, Dr. Baiyu Zhang for their guidance, inspiration, suggestions, criticism and financial support that they have provided throughout the course of my research and studies. Special thanks are also extended Dr. Zhendi Wang, who is in my supervisory committee and provided insight suggestions for this research. I also want to thank Tahir Husain and Dr. Yan Zhang for their helpful supervision during the program.

I also gratefully acknowledge the Faculty of Engineering and Applied Science, the Memorial University of Newfoundland (MUN), the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Foundation for Innovation (CFI), the Development Corporation of Newfoundland and Labrador (RDC), the Fisheries and Oceans Canada (DFO), the Environment and Climate Change Canada (ECCC), the Petroleum Research Newfoundland and Larbrador (PRNL), Suncor Energy, and Matics for their financial and/or technical support.

Additional gratitude is given to my colleagues Dr. Pu Li, Dr. Liang Jing, Dr. Jing Ping, Dr. Hongjing Wu, Bo Liu, Fuqiang Fan, Zelin Li, Tong Cao, He Zhang, Kedong Zhang, Xudong Ye, Xing Song, Qinhong Cai, Xiao Zheng, and Dr. Yinchen Ma for their friendship and assistance in the course of my research programme.

TABLE OF CONTENTS

List of Figures

List of Tables

List of Symbols and Abbreviations

ACE	Acenaphthene	IcdP	Indeno(1,2,3-cd)pyrene
ACY	Acenaphthylene	LOD	Limit of Detection
ANOVA	Analysis of Variance	NAP	Naphthalene
ANT	Anthracene	OFAT	One Factor a Time
AOPs	Advanced Oxidation Processes	PAHs	Polycyclic Aromatic Hydrocarbons
BaA	Benzo(a)anthracene	PHC	Petroleum Hydrocarbon
BaP	Benzo(a)pyrene	PHE	Phenanthrene
BbF	Benzo(b)fluoranthene	ppm	parts per million
BghiP	Benzo(g,h,i)pyrene	ppt	parts per thousand
BkF	Benzo(k)fluoranthene	PWRI	Produced Water Re-injection
CHR	Chrysene	PYR	Pyrene
DahA	Dibenzo(a,h)anthracene	SBSE	Stir Bar Sorptive Extraction
DOE	Design of Experiment	SPME	Solid Phase Micro-extraction
ER%	Extraction Recovery	TDS	Total Dissolved Solids
FLA	Fluoranthene	UDSA-DLLME	Up and Down Shaker Assisted-Dispersive Liquid-liquid Micro-extraction
FLO	Fluorene	UV	Ultraviolet

GC-MS	Gas Chromatography-Mass Spectroscopy	VSA-LLME	Vortex Shaker Assisted- Liquid-liquid Micro-extraction
HF-SDME	Hallow Fiber-Single Drop Micro-extraction	WLSEME	Water with Low concentration of Surfactant in Emulsion dispersive liquid–liquid Micro-extraction
OPW	Offshore Produced Water		

a	Interfacial area, cm^2
b	Path length, cm
$C_{A,0}$	Initial Concentration of Target Pollutant, M
C_{aq}	Concentration of Analyte in Water, M
$C_{A(t)}$	Concentration of Target Pollutant after treatment time t, M
C_i	Concentration of Matrix Specie i, M
C_{org}	Concentration of Analyte in organic phase, M
EF	Enrichment Factor
EY	Extraction Yield
He	Henry's Law Constant, $atm \cdot M^{-1}$
I_0	Irradiance Intensity, $Einstein \cdot L^{-1} \cdot s^{-1}$
k	First Order Reaction Constant, s^{-1}
k_c	Chemical Reaction Constant, $M^{-1} \cdot s^{-1}$
K_M	Ozone Absorptivity of Sample Water, $M^{-1} \cdot s^{-1} \cdot cm^2$
K_{PAH}	Ozone Reactivity of individual PAH, $M^{-1} \cdot s^{-1} \cdot cm^2$
Q	Flow Rate of Ozone Inlet, $L \cdot s^{-1}$
R	Removal Rate. %
r	Average Radius of Ozone Bubble, cm
t_r	Retention Time of Ozone Bubble Inside Sample Water, s
u	Velocity of Ozone Bubble Inside Sample Water, $cm \cdot s^{-1}$
V_{aq}	Volume of Aqueous Phase, ml
V_L	Volume of Water in Reactor, L
V_{org}	Volume of Organic Phase, ml
Z_{PAH}	Stoichiometric Factor of Target PAH

ε_A	Extinction Coefficient of Target Pollutant, $M^{-1} \cdot cm^{-1}$
ε_i	Extinction Coefficient of Matrix Specie i, $M^{-1} \cdot cm^{-1}$
Σ_{sample}	Attenuation Coefficient of Sample, cm^{-1}
$\Sigma_{sample,0}$	Initial Attenuation Coefficient of Sample, cm^{-1}
ϕ	Quantum Yields
ϕ_A	Quantum Yields of Target Specie
ϕ_D	Quantum Yields of PAHs in DD Water
ϕ_M	Hypothetic Quantum Yields of Matrix
$[O_3]$	Inlet Ozone Concentration, ppm
$[O_3]_g$	Gas Phase Ozone Concentration, ppm
$[O_3]_L$	Ozone Concentration in Water, M
$[O_3]_L^*$	Saturated Ozone Concentration in Water, M

CHAPTER 1 INTRODUCTION

1.1 Introduction

Produced water is the largest waste stream from oil and gas production (Boschee, 2012; McCormick, 2016; Prescott, Sankar, & Swenson, 2016; Szép & Kohlheb, 2010). The average volume of discharged water around the world can be as high as 210 million bbl per day or 77 billion bbl per year (Khatib & Verbeek, 2002). The sources of produced water usually include formation water, injection water, and treatment additives during drilling, stimulation, production, and oil-water separation processes (Fakhru'l-Razi *et al*., 2009). Various pollutants in produced water such as petroleum hydrocarbons (PHCs), metals, and other toxic chemicals can cause acute or chronic environmental problems if without proper treatment (Manfra *et al*., 2007). Thus, produced water management is a significant fraction of offshore production costs and requires various degrees of treatment before discharge or re-injection.

The major groups of organic (oil) compounds in produced water include aliphatic hydrocarbons, less soluble aromatic hydrocarbons, organic acids, and phenols. Depending on their solubility and partition, most aromatic hydrocarbons and aliphatic hydrocarbons exist in dispersed oil. Most contaminants in the dissolved oil (oil compounds completely mixed with water) are water soluble organic compounds such as organic acids and phenols. The dissolved oil also contains a considerable amount of toxic organic petroleum hydrocarbons such as polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, xylenes (BTEX), and alkylated phenols (APs) (Dórea *et al*., 2007).

Due to the considerable environmental impact caused by those contaminants, offshore produced water management has become one of the major concerns for offshore oil and

gas production. Since the last century, many studies have been conducted to improve policies and practices (Veil & Clark, 2011). Although some regarded produced water discharge as a low–impact operation due to the high rates of dilution by the receiving seawater (Bakke, Klungsøyr, & Sanni, 2013), chronic exposure to produced water could be induced by reef effects near offshore structures. More evidence about the toxicity of produced water and the bioaccumulative effects were observed with growing risks and impacts especially during the vulnerable development stages of marine organisms. Consequently regulatory requirements have become more stringent in the past decade, promoting and demanding more effective treatment technologies for offshore produced water management (Holdway, 2002; Jerry M. Neff, Johnsen, Frost, Røe Utvik, & Durell, 2006).

Among the contaminants in offshore produced water, PAHs are a group of petroleum hydrocarbons of the greatest environmental concern because of their well-known toxicity and persistence in the marine and coastal environments (Durell *et al*., 2006). Although solubility of PAHs is low and usually decreases with increasing molecular weight, their hazard potential even in trace amounts can be relatively high due to large amount of discharge and long-term bioaccumulation. Thus, their presence in the water cycle pose acute or chronic risks to the marine ecosystems and human health through food chains.

Besides the need of removal of PAHs from produced water discharge, onsite treatment is desirable in order to reduce shipping and handling costs, and potential risk of accidental releases during shipping, as well as growing health, safety and environmental concerns.

1.2 Statement of Problems

Current onsite treatment is mainly dependent upon techniques through which the bulk of oil is separated from the produced water to meet the regulatory standards (e.g., hydrocyclone and air floatation) (Liang Jing, Chen, & Zhang, 2014; Liang *et al*., 2014). They have low efficiency in the removal of the dissolved organic compounds in water phase including PAHs that make a significant contribution to the toxicity of the produced water (Z. Chen, Zhao, & Lee, 2010). Recently, some emerging techniques, such as membrane filtration, biofiltration, activated carbon adsorption, and oxidation processes, have been considered to remove dissolved oil and more dispersed oil in produced water to meet more stringent requirements (Haritash and Kaushik, 2009; Souza Duarte *et al.*, 2011; Alkhudhiri *et al.*, 2013; Igunnu and Chen, 2014; Liu *et al.*, 2014). However, most of them have various limitations that must be considered in developing onsite treatment technologies for installation and operation on offshore platforms or vessels (Hawboldt *et al.*, 2010). In offshore operations, weight and space of treatment facilities are the most severe constraints, so highly efficient and compact treatment systems with low water retention are much desired.

AOPs are a set of chemical treatment procedures to remove contamnants in water and wastewater through reaction with hydroxyl radicals. AOPs are capable of removing organic pollutants without chemical residues or secondary pollution. They have been apporved to have the strong capabilty of decomposing dissolved organic compounds including hydrocarbons in water (Walker *et al.*, 2001; Wang *et al.*, 2013; Klamerth *et al.*, 2015). Some AOPs such as photo-oxidation, ozonation and Fenton oxidation have already been widely

applied in the treatment of drinking water, municiple wastewater (Wang *et al.*, 2003; Hollender *et al.*, 2009; Rakness, 2011; Stalter *et al.*, 2011; Xu *et al.*, 2012; Antonopoulou *et al.*, 2014) and industrial wastewater effluents (Lin *et al.*, 2014; Rubio-Clemente *et al.*, 2014; Wu *et al.*, 2015). Furthermore, AOPs are also featured with high cost-efficiency, small footprints, and eco-friendliness which well match the requirements of offshore operation and present a promising treatment option for offshore produced water. However, some studies have reported low effeciency in some wastewater treatment cases due to changed water consitution (Fakhru'l-Razi *et al.*, 2009). Also, photo-oxidation of hydrocarbons has been documented to possibly increase toxicity in some cases (Stepnowski *et al.*, 2002). The complex chemical constitution in offshore porduced water can also sinificantly complicate the mechanisms of the treatment process. The oxidation process of PAHs may be significantly inhibited compared to AOP treatment of drinking water and municipal wastewater. In the past years, there have been limited research efforts on investigating the AOP oxidation kinetics and mechanisms of PAHs and evaluating the feasibility of using AOPs in offshore produced water treatment. Some important questions such as toxicity of treated effluent and impact on biodegradability remain unanswered. Establishing these knowledge is thus necessary and urgent for improving scientific understanding and promoting practical application of AOPs in offshore produced water treatment to support sustainable offshore development and protect marine and coastal environments.

1.3 Objectives

The objectives of this research are to develop advanced oxidation technologies for removal of PAHs from offshore produced water and examine their mechanisms, performance and applicability. The major research tasks include:

1) to develop batch- and bench-scale experimental systems for tersting advanced oxidation methods including UV photolysis, ozonation and photo-ozonation (UV/Ozone) for offshore produced water treatment;
2) to develop new analytical methods for fast, realiable and accurate dertermination of PAHs in offshore produced water;
3) to evaluate the effectiveness in removal of PAHs from offshore produced water and identify and quantify the influence of key operational factors;
4) to develop kinetic models and analyze mechanisms for the oxidation processes of PAHs in produced water under different conditions; and
5) to evaluate toxicity and biodegradability of the treated effluent by AOPs.

1.4 Structure of the Thesis

Chapter 2 provides a comprehensive review of produced water generation, properties, legislation, technologies, and practice for offshore produced water management and technical challenges.

Chapter 3 describes the development of Vortex and Shaker Assisted Liquid-liquid Micro-extraction (VSA-LLME) pretreatment method for determination of 16 PAHs in

offshore produced water. The optimization of VSA-LLME and sequential gas chromatography and mass spectrometry (GC-MS) analysis is also demonstrated by both one-factor a time (OFAT) and design of experiment (DOE) methodologies in this chapter. The performance of the analytical method is validated by experimental results.

Chapter 4 investigates the photooxidation process of PAHs in offshore produced water and evaluates the treatment performance. The effects of substrate and operational factors were disscussed. The mechanisms, especially including the dynamic competitiveness as a major mechanism of inhibition, are established, along with the description of the development of kinetics models.

Chapter 5 reports the behaviors of PAHs during ozonation and Ozone/UV treatment of offshore produced water. The effects of different operational factors are quantified. The major mechanisms associated with the offshore produced water substrate are discussed. The results of toxicity and biodegradability analysis are also presented in this chapter.

Chapter 6 summarizes the major results of this research as well as the scientific and practical contributions.

CHAPTER 2 LITERATURE REVIEW

The contents of this chapter are based and expanded on the following paper:

Jisi Zheng, Bing Chen, Worakanok Thanyamanta, Kelly Hawboldt, Baiyu Zhang, Bo Liu: *Offshore produced water management: A review of current practice and challenges in harsh/Arctic environments*. Marine Pollution Bulletin 01/2016; 104(1). DOI:10.1016/j.marpolbul.2016.01.004

Role: Jisi Zheng contributed most of the reviews and writing work under the supervision of Dr. Bing Chen and Dr. Kelly Hawboldt. Dr. Worakanok Thanyamanta, Dr. Bing Chen, and Dr. Kelly Hawboldt also provided some assistance on the literature reviewing and writings in certain sections.

2.1 Overview of Offshore Produced Water

Global energy demand continues to grow (Chu and Majumdar, 2012; Davidson *et al.*, 2014); and with it, oil and gas production experiences rapid increases to meet increased energy consumption. Offshore oil and gas production began in the 1940s in Louisiana's offshore region. Due to the development over the last six decades, large offshore reservoirs such as the offshore Alaska, Gulf of Mexico, the North Sea and the North Atlantic have been explored and well developed for production (Fraser, 2014). Offshore production accounts for 30 percent of the world's oil and gas production and is expected to increase in the future (Fakhru'l-Razi *et al.*, 2009). It is now moving into deeper waters and harsher environments such as the Arctic, which represents a new set of challenges for safe and environmentally sound operations (Gautier *et al.*, 2009; Harsem *et al.*, 2011) .

Produced water is the largest volume of the waste stream from oil and gas production (Veil *et al.*, 2004; Ranck *et al.*, 2005; Clark and Veil, 2009; Mastouri and Nadim, 2010; Dos Santos *et al.*, 2014). It is a mixture of formation water, re-injected water, and treatment chemicals during drilling, stimulation, production, and oil-water separation processes (Neff *et al.*, 2011). The effluent usually contains various pollutants such as petroleum hydrocarbons, metals, heavy metals, toxic treatment chemicals, which may result in unexpected environmental issues (Stephenson, 1992b; Fakhru'l-Razi *et al.*, 2009; Shpiner *et al.*, 2009; Barker and Jones, 2013). Since tens of millions of barrels of offshore produced water are generated daily worldwide (Fakhru'l-Razi *et al.*, 2009), the environmental impact brought by the contaminants in the effluent has become a major concern for the oil and gas industry and government, thus promoting the significance of offshore produced water

management. The major strategies for offshore produced water management includes water minimization, water reuse and water disposal (Veil and Clark, 2011). Both water reuse and discharge require treatment processes to meet certain regulatory standards or technical requirements. Only a small part of the water is reused by re-injection in offshore production and most offshore produced water is surface discharged for disposal. For instance, only 8.3 percent of offshore produced water generated in the United States was re-injected for enhancing recovery and 91.5 percent of water was surface discharged to the ocean in 2007 (Clark and Veil, 2009). Weight and space are the most critical constraints in current offshore treatment practices; thus, only compact technologies with low water retention are appropriate for offshore platforms.

Harsh environments refer to warm and cold climatic conditions that are difficult for people to work in and for process plants to be operated (Khan *et al.*, 2015). The Arctic and the sub-Arctic region are in one of the harshest environmental conditions in the world. Considerable offshore oil and gas production is in harsh and Arctic environments which can bring cold temperatures, fragile ecosystems, and in some cases require unmanned operations adding further complexity to produced water management (Jing *et al.*, 2012). In such environments, more severe contaminant reduction is necessary (Noble *et al.*, 2013). Various emerging technologies which can be applied onshore, however, can raise installation and operation issues offshore and thus limit their applicability in harsh/Arctic environments.

Currently, there are very few studies dedicated to offshore produced water management and specifically for harsh/Arctic environments. Thus, management of offshore produced water and reduction of environmental impacts that efficiently tackles

the challenges in such highly vulnerable environments has become urgent tasks. Therefore, in this chapter, produced water status and its characteristics from offshore oil and gas production are outlined. This chapter also summarizes current management policies for offshore produced water. The current offshore produced water treatment technologies were discussed to show their feasibilities and potentials, especially for application in harsh/Arctic environments. The biggest challenges for management in harsh/Arctic environments are also demonstrated. This chapter represents a comprehensive study of offshore produced water management and its challenges in harsh/Arctic environments. The priorities for future research and development for offshore produced water management in harsh/Arctic environments are also highlighted.

2.1.1 Offshore Produced Water Production Status

Offshore produced water is generated through the production of oil and gas from offshore wells. The primary source of offshore produced water is formation water. For offshore wells, formation water is usually the seawater that has been trapped with oil and gas in an offshore reservoir (Collins, 1975), so the salinity of the produced water may reach a level higher than seawater (**Table 2.1**). It may contain the flows from above or below the hydrocarbon as well as the flow from within the hydrocarbon zone (Fakhru'l-Razi *et al.*, 2009); therefore, the offshore produced water always contains a significant amount of petroleum hydrocarbons and related organic pollutants. Also, surface water and production chemicals are sometimes injected into the reservoir to enhance production. These injected waters can also penetrate the production zone and get produced with oil and gas (Frid, 2003; Veil *et al.*, 2004). The topsides are designed to separate produced water from the petroleum

fluids (Ekins *et al.*, 2007). After separation, a small amount of dispersed and dissolved oil may remain in the water that requires further treatment for re-injection or discharge.

2.1.2 Production Volume

Produced water represents the largest waste effluent volume for most offshore platforms (Stephenson, 1992b; Krause, 1995). On a global scale, the water to oil ratio is approximately 3:1 for oil producing wells, and is higher for gas wells (Neff *et al.*, 2011). As shown in **Figure 2.1**, offshore production volumes are significant but currently lower than onshore. However, the fraction of offshore production volume is increasing, indicating the growing importance of handling offshore produced water. Volumes of produced waters vary from site to site. The differences in volume, as well as the characteristics of produced water, depend on many parameters including the age of field, geographic location, reservoir type, and production technologies. As also shown in **Figure 2.1**, the volume of produced water typically increases as production ages (Clark and Veil, 2009). With maturing fields and new fields, water volume tends to increase each year leading to a higher volume of wastes to be handled (Henderson *et al.*, 1999). Some data on offshore oil and water production for some large oil fields in harsh environments are summarized in **Table 2.1**. From this Table, the water/oil ratios are around 3:1 but different from site to site. The high production rates of produced water discharged offshore can result in significant environmental risks. As exploration expands to colder environments such as the Arctic, the discharge of such amounts of produced water from platforms will bring greater concerns for the receiving environment and therefore reduction in volume and managing environmental impacts has become even more crucial (Casper, 2009). Therefore, more

stringent environmental policies have been proposed such as “zero discharge” policies due to the higher vulnerability (Smit *et al.*, 2011).

2.1.3 Contaminants and Toxicity

Offshore produced water contains various organic and inorganic substances from geologic formations. Stephenson (Stephenson, 1992a) categorized produced water constituents into oil (organic compounds), salt, dissolved oxygen, heavy metals, radionuclides, and treatment chemicals. Other contaminants, such as production solids and dissolved gasses are also present (Hansen and Davies, 1994; Fakhru'l-Razi *et al.*, 2009). The produced water also contains bacteria (Yeung *et al.*, 2011). In general, the properties of produced water have larger variability than those of seawater, raising significant environmental concerns (**Table 2.2**). These properties depend on the nature and conditions of the reservoir, type and conditions of the production process, and environmental conditions.

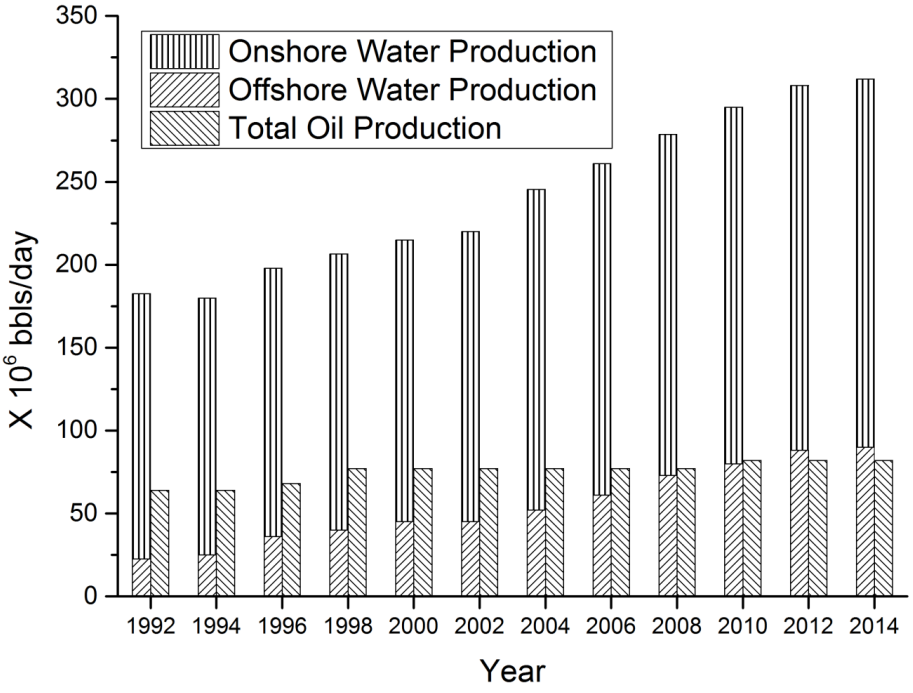


Figure 2.1 Global oil and water production
(Fakhru'l-Razi *et al.*, 2009; NETL, 2013)

Table 2.1 Offshore oil and gas produced water production data from oilfields in harsh environments

Offshore Oil Field	Annual production			Water to Oil Ratio	Ref.
	Oil (10^6 m^3)	Gas (10^6 m^3)	Water (10^6 m^3)	Water/Oil (m^3/m^3)	
Hibernia (North Atlantic)	15.4	3,889	58.5	3.8	(CAPP, 2001)
Alaska (Cook Inlet)	41.8	4,700	121	2.9	(Clark and Veil, 2009)
North Sea (Demark)	11.3	8,556	34.2	3	(MAERSK, 2011)
North Sea (Norway)	84	62,000	200	2.4	(Directorate, 2011)

The major groups of oil compounds in produced water include aliphatic hydrocarbons, aromatic hydrocarbons, organic acids, and phenols. Depending on the solubility and partition, most aromatic hydrocarbons and aliphatic hydrocarbons are in the dispersed oil. Most contaminants in dissolved oil are water soluble organic compounds such as organic acids and phenols. It should be noted that, although most petroleum hydrocarbons are in dispersed oil, the dissolved oil still contains a considerable amount of toxic organic petroleum hydrocarbons such as BTEX, polycyclic aromatic hydrocarbons (PAHs) and alkylated phenols (APs) (Dórea *et al.*, 2007). The concentrations of these compounds in offshore produced water also depend on parameters such as the volume of water produced, the production technique and production age (Stephenson, 1992b). Among the most toxic components in produced water, PAHs and some APs with higher molecular weights are less water soluble and thus partition themselves in dispersed oil (Ekins *et al.*, 2007). PAHs and C_6 - C_9 APs have strong correlations with dispersed oil content (Faksness *et al.*, 2004). The type of reservoir is one of the main factors in the composition of the dissolved fraction. From gas condensate fields, high levels of phenols and low–molecular–weight aromatics take place leading to a high degree of toxicity.

A substantial amount of dispersed oil is removed by some oil/water separation processes. During oil/water separation, free oil, and larger oil droplets are removed. Small droplets or emulsified oil remain in the water phase are discharged into the seawater. The dissolved oil fraction is harder to remove than the dispersed fraction. The amount of the soluble oil fraction depends on oil composition as well as oil and water properties. Dissolved organics increase with pH and temperature while pressure has little effect on solubility (Fakhru'l-Razi *et al.*, 2009). Fatty acids are the most abundant compounds in the

dissolved oil fraction (Somerville *et al.*, 1987; Barth, 1991). The concentrations of these organic acids in produced water are inversely proportional to their molecular weights (Utvik, 1999). Even though the concentration of phenols is low, the APs have a high fat affinity and therefore tend to be bio-accumulate in animal tissue, and have lower degradability than their parent phenols (Boitsov *et al.*, 2007). The dominant toxic petroleum hydrocarbons in the soluble fraction are volatile aromatics and naphthalenes (Brendehaug *et al.*, 1992). Among those dissolved compounds, PAHs are considered to be the largest contributor to offshore produced water toxicity (Neff *et al.*, 2006). **Table 2.3** summarizes the concentrations and fractions of PAHs for three offshore oilfields in harsh environments. The data show that considerable amounts of PAHs are present in discharge effluents, exhibiting significant variability from site to site. Both parent PAHs and alkyl PAHs can dominate the total PAHs content. This variance could be caused by factors such as oil constitution, the production process, and treatment efficiency. Most PAHs in produced waters have low molecular weights (mostly two rings and three rings) due to their higher solubilities. Heavier (3–6 rings) PAHs are less water soluble and thus, are present mainly in the dispersed oil phase. The fraction of parent PAHs for the Grand Bank is lower, so that the the toxicity is majorly lower than the Gulf of Mexico and comparable to North Sea. The parent PAHs especially the more rings the PAH specie has, the higher persistence and toxicity it has. Since the Grand Bank has higher more-rings PAHs, for example, Chrysene, the long-term impact of the Grand Bank could be a greater concern compare to the other two sites especially when it is located in lower-temperature location. Recently, petroleum hydrocarbons in produced water are typically measured as oil and grease which is used as the main parameter in developing the produced water regulatory discharge limits. These

terms are ambiguous because most of the hydrocarbons are partially water soluble with different levels of solubility and different partition coefficients for extraction solvent. Therefore, the constituents of measured oil and grease may not include some fraction of the dissolved oil phase but may include some non-hydrocarbon inorganic compounds (Romero and Ferrer, 1999).

Produced water also contains various inorganic species with significantly higher concentration than seawater (**Table 2.2**). Salts are the largest constituents in produced water (**Table 2.2**). These include sodium and other dissolved ions such as calcium, magnesium, and potassium. Similar to seawater, sodium, and chloride contributes the most to produced water salinity while calcium, magnesium, and potassium play less important roles. Measured regarding total dissolved solids (TDS), the values vary by location ranging from 100 to more than 300,000 mg/L (**Table 2.2**), compared with the salinity around 35,000 mg/L of seawater. Compared to seawater, the most abundant metals in produced water samples are sodium, calcium, magnesium, and potassium. However, most of these are less toxic. More toxic metals (primary pollutant metals) cadmium, cobalt, copper, lead, mercury, and nickel are found less frequently and in lower concentrations. Naturally occurring radioactive materials (NORMs) sourced from geologic formations can be found in produced water. The amount and types of radioactive substances depend on their geologic formations. The most common are Radium, ^{226}Radium, and ^{228}Radium. The concentrations found in the North Sea samples ranged from below detectable levels (0.3 and 1.3 Bq/L) to levels between 16 and 21 Bq/L for ^{226}Ra and^{228} Ra (Hamlat *et al.*, 2001; Robinson, 2013). Theses concentration levels may generate serious concerns (Veil *et al.*, 2004). In addition to the naturally existing compounds, treatment chemicals are added to aid in the production

processes or produced oil/water separation processes. These include scale inhibitors, corrosion inhibitors, biocides, emulsion breakers, and well stimulation chemicals. Their species are summarized in **Table 2.4**. This Table also shows there is no significant difference between the consumption rates of each chemical species for the North Sea and the Gulf of Mexico, which sugguest that colder environments do not require fewer treatment chemicals for production. The reason can be that the production temperature being maintained at a much higher level so that the ambient temperature does not have a major influence.

As produced water may pose significant adverse impacts to the marine environment (Middleditch, 1984; Holdway, 2002; Manfra *et al.*, 2007; Pérez-Casanova *et al.*, 2010; Van Scoy *et al.*, 2010), its environmental risk is a serious concern. The EC_{50} of offshore produced water in harsh environments varies from location to location. The values for the Grand Banks ranges from > 5-10% while values between 3.5-6.3% were found for the North Sea platforms (Stagg and McIntosh, 1996; Lee *et al.*, 2011). Nonpolar organics are considered more toxic as they are lipophilic (Elias‐Samlalsingh and Agard, 2004) while aromatic hydrocarbons contribute the most to produced water toxicity (Shiu *et al.*, 1990). It has been found from recent studies that the dissolved fractions of PAHs and APs are contaminants of most concern regarding the acute and chronic toxicity of produced water (Boese *et al.*, 1998; Faksness *et al.*, 2004; Michałowicz and Duda, 2007; Carls *et al.*, 2008). Even though organic acids account for the highest fraction of produced water, they are considered “non–hazardous” (Brendehaug *et al.*, 1992). Treatment chemicals present in produced water may increase the toxicity risk posed by dispersed oil by changing

contaminant phase partitioning (Henderson *et al.*, 1999; Neff *et al.*, 2006). For example, surfactants reduce interfacial tension between oil droplets and water making separation more difficult, which may lead to higher amounts of dispersed oil in produced water, and the hydrocarbons may also be more readily available to marine organisms (Frid, 2003; McIntosh *et al.*, 2010; Zuijdgeest and Huettel, 2012). Produced waters from gas platforms are typically more toxic due to their higher levels of aromatic hydrocarbons (Orem *et al.*, 2007; Neff *et al.*, 2011; Lourenço *et al.*, 2013).

2.2 Policy and Regulations

Many discharge guidelines have been developed to address technical, environmental, and economic issues. The US Environmental Protection Agency (EPA) has developed two produced water discharge limits, namely technology-based and water-quality-based limits. For oil and gas extraction operations, effluent limit guidelines (ELGs) found on BATs (defined by the EPA as Best Available Technology Economically Achievable) focus on oil and grease in produced water. The limits for oil and grease are 29 mg/L monthly average and 42 mg/L daily maximum based on air flotation technology. In addition to the national oil and grease limits, there are also regional limits such as flow rate, toxicity testing, and monitoring requirements for several toxic metals, organics, and naturally occurring radioactive materials. These limits vary depending on the characteristics and vulnerability of each area. The EPA regional office in Region 10 covers discharges in harsh/Arctic environments, including the Cook Inlet and the Arctic. Cook Inlet, Alaska is the only coastal

area in the US that allows discharge of produced water (NETL, 2010).

Table 2.2 Summary of produced water chemical composition
([a]Collins, 1975; [b]Tibbetts *et al.*, 1992; [c]Neff, 2002; [d]Ekins *et al.*, 2007; [e]Neff *et al.*, 2011; [f]Sharqawy *et al.*, 2011; [g]Bhadja and Kundu, 2012)

Parameter	Seawater		Produced Water	
	Range/median	**Unit**	**Range**	**Unit**
Density	~1.025[a]	kg/m^3	1.014-1.14[a]	kg/m^3
Surface Tension	70-77[b]	dynes/cm	43-78[b]	dynes/cm
pH	7.5-8.4[a]		4.3-10[a]	
Salinity (TDS)	~35[g]	g/L	<0.1 - >300[g]	g/L
COD	~1[b]	mg/L	1220[b]	mg/L
Chloride	~19353[a]	mg/L	46,100-14,100[a]	mg/L
Sulfate	~2712[a]	mg/L	210-1,170[a]	mg/L
Bromide	~87[a]	mg/L	46-1,200[a]	mg/L
Ammonium	–	mg/L	23-300[c]	mg/L
Bicarbonate	~142[a]	mg/L	77-560[a]	mg/L
Iodide	~167[a]	mg/L	3-210[a]	mg/L
Carbonate	–	mg/L	30-450[c]	mg/L
Metals				
Boron	~4.45[d]	mg/L	8-40[d]	mg/L
Lithium	~0.17[d]	mg/L	3-50[d]	mg/L
Sodium	~10,760[d]	mg/L	23,000-57,300[d]	mg/L
Calcium	~416[d]	mg/L	2,530-25,800[d]	mg/L
Magnesium	~1,294[d]	mg/L	530-4,300[d]	mg/L
Potassium	387[d]	mg/L	130-3,100[d]	mg/L
Strontium	~0.008[d]	mg/L	7-1,000[d]	mg/L
Barium (Ba)	22–80[d]	µg/L	0.2–228[d]	mg/L
Cadmium (Cd)	4–23[d]	ng/L	0.5–5[d]	µg/L
Copper (Cu)	20–500[d]	ng/L	22–82[d]	µg/L

Mercury (Hg)	1–3 [d]	ng/L	<0.1–26 [d]	µg/L
Lead (Pd)	20–81 [d]	ng/L	0.4–8.3 [d]	µg/L
Zinc (Zn)	0.3–1.4 [d]	µg/L	0.5–13 [d]	mg/L
Iron(FeII)	1.8 [d]	µg/L	0.1–15 [d]	mg/L
Iron(FeIII)	–	–	4.5–6 [d]	mg/L
Radium (226 RA)	–	–	1.66[e]	Bq/L
Radium (228 RA)	–	–	3.9 [e]	Bq/L
Manganese (Mn)	–	–	0.1–0.5 [e]	mg/L
Beryllium (Be)	–	–	0.02 [e]	mg/L
Nickel (Ni)	–	–	0.02–0.3 [e]	mg/L
Cobalt (Co)	–	–	0.3–1 [e]	mg/L
Vanadium (V)	–	–	0.02–0.5 [e]	mg/L
Total Organic Carbon[f]	–	–	<0.1->11,000	mg/L
BTEX	–	–	0.068-578	mg/L
PAH	1–45	ng/L	40-3,000	µg/L
Organic Acids (<C_6)	–	–	<0.001-10,000	mg/L
Phenols(C_0–C_5)	–	–	0.4–23	mg/L

Table 2.3 PAHs concentrations for typical oilfields in harsh environments
(Neff, 2002; Neff *et al.*, 2011)

	Grand Bank	Scotian Shelf	North Sea
Total PAHs (µg/L)	2148.63	886.35	N/A
Fraction of Akyl PAHs (%)	78.90	28.70	N/A
Fraction of NPD (%)	18.97	70.58	N/A
Fraction of EPA 16 PAHs (%)	21.00	71.28	N/A
Total EPA 16 PAHs (µg/L)	186.12	1531.63	132.32
Fraction of included NPD species (%)	86.13	98.98	89.71
Fraction of other parent PAHs (%)	13.87	1.02	10.29
Other Parent PAHs (µg/L)	25.82	15.63	13.62
Fluorene %	63.90	83.17	49.19
Acenaphthylene %	8.91	8.32	17.25
Acenaphthalene %	0.00	0.00	13.07
Anthrancene %	0.00	1.66	8.59
Fluoranthene %	1.98	2.50	2.13
Pyrene %	3.64	2.30	3.45
Benz(a)antharancene %	2.32	2.05	1.84
Chrysene %	13.94	0.00	3.82
Benz(b)fluoranthene %	2.36	0.00	0.23
Benz(k)fluoranthene %	0.00	0.00	0.05
Benz(a)pyrene %	1.47	0.00	0.16
Indeno(1,2,3-cd)pyrene %	0.00	0.00	0.04
Dibenz(a,b)anthracene %	0.81	0.00	0.04
Benz(g,h,i)perylene %	0.66	0.00	0.14

Table 2.4 Summary of production chemicals in offshore produced water
(CAPP, 2001; Johnsen *et al.*, 2004)

Function	Chemical class	Primary solubility	Treatment conc. (ppm)	
			North Sea	The Gulf of Mexico
Corrosion Inhibitor (acid)	Amine imidazolines	Oil	25-100	25 –100
	Amines	Oil		
	Amine salts	Water		
	Quaternary ammonium salts	Water		
	Nitrogen Heterocyclics	Oil		
Corrosion Inhibitor (oxygen)	Ammonium bisulfite	Water	5-15	5-15
Bactericide	Quaternary amine salt	Water	10-200	N/A
	Amine acetate	Water		<30 continuous
	Glutaraldehyde	Water		<200 batch
Hydrate Inhibitor	Methanol	Water	N/A	5-15 gal/mmcf
	Ethylene glycol	Water	N/A	<10 gal/mmcf
Dehydration	Triethylene glycol	Water	N/A	N/A
Scale Inhibitor	Phosphate esters	Water	3-10	3-10
	Phosphonates	Water		
Emulsion Breaker	Oxyalkylated resins	Oil	10-200	<30
	Polyglycerol esters	Oil		
	Sulfonates	Oil		
Solid	Polyamine	Water	<3	<3

removal	Quaternary polyamine	Water

The regulations for ocean discharge of oil and gas production wastes in the North Sea are the most developed. The Convention for the Protection of Marine Environments of the North-East Atlantic (OSPAR Convention) has issued a recommendation for management of produced water from offshore. The recommendation focuses on applying the latest technological developments and practices through the use of BATs (defined by OSPAR as Best Available Techniques) and Best Environmental Practice (BEP). OSPAR also takes steps forward to achieve long-term elimination of pollutants in produced water. Also, the recommendation also ensures an "integrated approach" where reduction in marine discharge does not pose impacts to other environmental sectors. Discharge minimization and "zero discharge" practices should be considered in new and substantially modified installations. For ocean discharges, the regulations require a performance standard for dispersed oil of 30 mg/L for produced water. The performance standard according to the OSPAR Recommendation is defined as a limit value for a concentration in mg/L, calculated on the basis of the total weight of the relevant substances discharged per month, divided by the total volume of water discharged during the same period (Tromp and Wieriks, 1994).

Offshore discharges of produced water in Canada occur at production sites in the Atlantic region. The two major regulating authorities are the Canada-Newfoundland & Labrador Offshore Petroleum Board (C-NLOPB) and the Canada-Nova Scotia Offshore Petroleum Board (CNSOPB). The Offshore Waste Treatment Guidelines (2010) were developed jointly by the National Energy Board (NEB), the C-NLOPB, and the CNSOPB (NEB *et al.*, 2010). The guidelines apply to oil and gas development activities in Canada's offshore areas. In Newfoundland, the guidelines are administered under the Canada–Newfoundland Atlantic Accord Implementation (Newfoundland) Act and in Nova Scotia,

under the Canada-Nova Scotia Atlantic Offshore Petroleum Resources Accord Implementation Act. Meanwhile, two types of monitoring programs are required. One is the compliance monitoring program to measure the quality of the discharged stream. Where applicable, the measurements or calculations of absolute quantities of oil-in-water or other contaminants should be included in the program. The other is the environmental effects monitoring program to assess and document any environmental impacts that might result from the discharge.

By comparing different policies and standards worldwide, it may be concluded that more stringent policies are implemented in higher latitude areas such as the North Atlantic, North Sea and Alaska (**Table 2.5**). The North Sea and North Atlantic have much more strigent standards than tropical oilfields such as those in Miditerranean, Red Sea and South-east Asia. Since the oilfields in harsh environments have higher chances for exposure to harsh environments may pose a higher vulnerability for produced water discharge. Thus, more stringent policies are applied. Impact assessment targeting such areas has become crucial. However, limited environmental impact assessment studies have been conducted in these regions. In the future, more stringent policies may be proposed for further development in colder regions such as the Arctic, as more environmental research are conducted in this region.

Table 2.5 Regulations and discharge standards of oil and grease concentration for offshore produced water discharge worldwide

Region	Latitude	Legal Base	Standard	
			Daily Max.	Ave.
Europe				
North Sea	High	OSPAR Convention (Tromp and Wieriks, 1994)	–	30 mg/L
Baltic Sea	High	HELCOM Convention (HELCOM, 2007)	15 mg/L	–
Mediterranean	Low	Barcelona Convention (Pavasovic, 1996)	100mg/L	40 mg/L
Asia				
Red Sea	Low	KUWAIT Convention (Mahmoudi, 1997)	100 mg/L	40 mg/L
China	Moderate	GB 4914-85	70 mg/L	30-50 mg/L
Indonesia	Low	MD KEP 3/91; 42/97	100 mg/L	75 mg/L
Thailand	Low	NEQA 1992: Gov. Reg. 20/90	100 mg/L	40 mg/L
Vietnam	Low	Decision No. 333/QB 1990	–	40 mg/L
North America				
United States (Alaska)	High	40 CFR 435	42 mg/L	29 mg/L
Canada (North Atlantic)	High	Act RSC 1987	60 mg/L	30 mg/L
South America				
Brazil	Moderate	–	20 mg/L	–
Oceania				
Australia	Moderate	–	50 mg/L	30 mg/L

2.3 Offshore Produced Water Management Technologies

The primary differences in managing produced water offshore and onshore are a result of space and weight limitations and motion on offshore platforms. Factors such as different regulations, produced water volume, and alternative sources of water for water-flooding also lead to various options for onshore and offshore produced water management. The targeted contaminants are also different. For onshore water management, reduction of salt is required before discharge while offshore, oil and grease levels are a major concern (Otton, 2006). These factors lead to different directions in treatment technologies. For example, to remove salts and inorganic components, reverse osmosis, deionizing techniques (ion exchange or capacitive deionizing), and thermal treatments (e.g. distillation) are used. Technologies that require large spaces and long retention times, especially during sedimentation and biological treatment are widely used onshore. Transportation of consumables or chemicals also limits the use of complex treatment systems on offshore platforms. Limited space for offshore production restricts treatment system size, which in turn affects treatment efficiency. Moreover, in remote areas or harsh environments, low–maintenance or even unmanned facilities may be necessary. This further restricts water management options and effectiveness considering the difficulties in regular monitoring of remotely operated or automatically controlled treatment equipment and water discharge.

2.3.1 Water Minimization

Reducing the volume of water produced not only allows more oil to be produced (for the same volume of fluid produced) but also decreases the cost of lifting a heavier fluid to

the surface. Moreover, costs of equipment maintenance and produced water handling and treatment are greatly reduced. From an environmental point of view, less amount of chemicals are used for water separation and less volume of produced water and associated pollutants are discharged into the ocean. To mechanically block water from entering the well, various mechanical devices such as straddle packers, bridge plugs, tubing patches, and cement are used (Seright *et al.*, 2001; Hayes and Arthur, 2004). The effectiveness of mechanical blocking techniques depends on the type of reservoir and well construction. Chemicals are also used to shut off water-bearing channels or fractures within the formation (Mitchell and Salvo, 1990; Nasr-El-Din and Taylor, 2005; Al-Muntasheri *et al.*, 2007; Simjoo *et al.*, 2009; Al-Muntasheri *et al.*, 2010; Shafian *et al.*, 2010). Shahab et al. provided a case that reduced the water cut by 2%-12% by with the application of an organic polymer (Chen *et al.*, 2014), while Qing et al. suggested that a 20%-50% reduction of the water cut can be achieved with foam gel (Qing *et al.*, 2009). However, this technique requires chemical additions which are difficult to remove. A reduction in produced water volume can also be obtained by downhole oil/water separation (DOWS) which usually involves using a hydrocyclone to separate water and oil inside the well space (Bybee, 2005; Dong *et al.*, 2011; Amini *et al.*, 2012). This technique is restricted to suitable wells and water injection zones. Seafloor separation technologies are very similar to topside water treatments. However, because the treatment unit sits at the bottom of the ocean, it eliminates issues of the limited space and weight burden that are usually found in topside installations (Bringedal *et al.*, 1999). However, subsea systems are expensive, and the industry has limited experience in implementing this technology.

2.3.2 Produced Water Re-injection

Produced water does not have as a wide utilization offshore as it does onshore. For onshore practice, treated water can be used for irrigation or cleaning purpose (Hillie and Hlophe, 2007; Fakhru'l-Razi *et al.*, 2010; Shaffer *et al.*, 2013). For offshore operations, the primary reuse of produced water is to enhance oil production. Water reinjection is a well-proven technology that has been the most common management practice for onshore produced water, mostly for improving oil recovery (Bachman *et al.*, 2003; Wang *et al.*, 2008; Voordouw *et al.*, 2011). Even though the water is to be reinjected, various treatments at the surface facilities to meet certain quality levels are required to prevent plugging wellbore and reservoir pores and avoid system failure. When the system fails, water needs to be discharged into the ocean. Factors limiting injection include dispersed oil, suspended solids, fatty acids, dissolved gasses, salts, pH, and the temperature of produced water. Moreover, compared to seawater, the utilization of produced water is much more challenging and expensive (Bader, 2007). Therefore, discharge is still considered the method that provides the highest level of management. The re-injected produced water is thus only a small part of the generated offshore produced water. For instance, only 8.3% of offshore produced water in the U.S. was re-injected for enhancing recovery in 2007 (Clark and Veil, 2009). In the North Sea Denmark, only 25% of offshore produced water is re-injected for both disposal and recovery enhancement (MAERSK, 2011).

2.3.3 Offshore Produced Water Treatment Technologies

A water treatment system may consist of a number of treatment stages and technologies. The skim tank, gas flotation/degasser and hydrocyclone are the frequently used primary

treatment techniques (Rhee *et al.*, 1989). These physical technologies target on dispersed oil. Emulsified oil and smaller oil droplets require more advanced techniques to achieve desired water quality levels. As discharge regulations can be more stringent due to the increased vulnerability in harsh/Arctic environments, emerging technologies that are capable of removing dissolved oil are desired.

Due to the increased concerns of the toxicity risks of dissolved oil and smaller dispersed oil droplets, emerging technologies are considered secondary treatment or polishing units. They often need to be used in combination with other currently used treatment systems such as hydrocyclone or flotation since high levels of dispersed oil or solids may foul secondary treatment equipment and decrease efficiency. Detailed information and discussion about those technologies are provided in **Table 2.6**. Among the emerging technologies, centrifuges provide much stronger centrifugal forces than hydrocyclones (via the rapid spinning bowl) and therefore can remove smaller oil droplets than a hydrocyclone (Ekins *et al.*, 2005). However, the higher energy and maintenance costs are required though the centrifuges can reach high flow capacity (Fakhru'l-Razi *et al.*, 2009). Coalescers merge small oil droplets into larger droplets to improve efficiency in other oil removal processes. Fine meshed media can coalesce smaller droplets but are more susceptible to fouling (Multon and Viraraghavan, 2006). This technology can only be applied in conjunction with other physical filtration techniques (Deng *et al.*, 2005; Multon and Viraraghavan, 2006). Physical filtration systems for offshore produced water treatment using sand, walnut shells, and multimedia (anthracite and garnet) have been employed (Adewumi *et al.*, 1992). However, the application of this technique on offshore platforms is significantly limited by their longer water retentions. Membrane filtration processes

remove suspended and dissolved particles that are larger than the membrane pore size. Oil droplets with sizes up to 0.01 microns can be removed. These processes have been used more widely in onshore oil fields to remove salts. Membrane filtration often requires multi-stage operations, and pre-treatment is usually required to remove larger substances. Chemicals may be added in the pre-treatment stage (Liangxiong *et al.*, 2003; Mondal and Wickramasinghe, 2008; Fakhru'l-Razi *et al.*, 2010; Alkhudhiri *et al.*, 2013; Alzahrani *et al.*, 2013). Fouling and requirements of space and weight capacity can be this technology's biggest limitations on offshore applications. Solids adsorption can be quite effective in removing most oil and other organic materials from produced water. In an adsorption process, molecules of contaminants adhere to the surface of solid media (adsorbents). Adsorption is used as a polishing step to avoid contaminant loads on adsorbents. Adsorption medias commonly used include organoclay, activated carbon, and zeolite (Altare *et al.*, 2007). Zeolite has recently been integrated with membrane technologies to achieve higher efficiency (Bowen *et al.*, 2004; Liu *et al.*, 2008; Kazemimoghadam, 2010). However, cost is a major concern of this kind of technology while high retention of water also limits its application. Freeze-thaw evaporation (FTE) is a mature and robust technology for produced water treatment which was developed in 1992 (Boyson and Boyson, 2004). The freezing point of water is usually higher than the contaminants in produced water. Therefore, FTE can allow relatively pure ice to be generated, resulting in a high concentration of dissolved contaminants in the remaining solution. This technique requires a large space and can only apply in a suitable area and environment. Chemical oxidation (e.g., ozone and hydrogen peroxide) is a traditional means of treating water and wastewater (Chang *et al.*, 2001; Canonica *et al.*, 2008; Broséus *et al.*, 2009; Oneby *et al.*, 2010; Margot *et al.*, 2013). The

very recent research found that enhanced oxidation by ultraviolet could lead to positive results particularly in produced water treatment (Jing *et al.*, 2014a; Jing *et al.*, 2014b; Jing *et al.*, 2015). The method can be used to remove dissolved residue and free oil within produced water before disposal by converting the hydrocarbons to carbon dioxide and water. The subsequent use of UV radiation and ozone oxidation may result in a positively synergistic effect for destroying organic contaminants. Research also demonstrated that while natural microbial populations in seawater partially biodegrade oil when sufficient nutrients were supplied, pre-treatment with photo-oxidation increased the amount of crude oil components susceptible to biodegradation, leading to significantly increased biodegradation of hydrocarbons (Stepnowski *et al.*, 2002). However, the reaction dynamics of the combination of ozone and ultraviolet are unclear, and it is questionable whether the process is fundamentally different from either ozone or UV treatment alone in such a wastewater with high salinity and high concentration of organic compounds. Also, photo-oxidation of hydrocarbons has sometimes been documented to possibly increase toxicity due to photo-transformation (Stepnowski *et al.*, 2002). Further research is still highly demanded to investigate the treatment efficiency and the associated risk or toxicity effects of photo-oxidation in combination or on their own on produced water. Regarding the detailed information for each technology in **Table 2.6**, it can be concluded that the application of most technologies is either significantly limited by the offshore application or challenges arise from harsh/Arctic environments.

Table 2.6 Summary of treatment technologies for offshore produced water treatment

Management	Efficiency/reduction		Typical cost (in 2013)		Feasibility for offshore application	Advantages	Disadvantages	Remarks for offshore and Harsh/Arctic environments application
	Dispersed oil	Dissolved Oil	Capital (hr/m^3)	Operational				
DOWS (Veil *et al.*, 2004; Zhang *et al.*, 2009; Amini *et al.*, 2012; OSPAR, 2013)	Yes	Yes	$14,000 (recent) $8,000 (new)	$1,603/kg dissolved oil $77/kg dispersed oil	No capacity limit; Low weight and space consumption	Less requirement for weight and space; reduction of water cut up to 50%	Restricted application on suitable well and water injection zone; mostly applied to onshore productions	Mostly applied onshore; No specific impact caused in Harsh/Arctic Environments
Water shut-off (chemical) (Sadarta *et al.*, 2000; Banerjee *et al.*, 2008; Simjoo *et al.*, 2009; Al-Muntasheri *et al.*, 2010; OSPAR, 2013)	Yes	Yes	$942-3,262	$87-3,705/kg dissolved oil $5.2-5,557/kg dispersed oil	No capacity limit; Low weight and space consumption	Direct reduction of water cut; less requirement for weight and space; reduction of water cut up to 50%; feasible for offshore production	Application of chemicals which are difficult to remove	Applied offshore; No specific impact caused in Harsh/Arctic Environments
Hydrocyclone (Choi, 1990; Fakhru'l-Razi *et al.*, 2009; Souza *et al.*, 2012; OSPAR, 2013)	Yes	No	$5,000 (recent) $3,660 (new)	$24-42/kg dispersed oil	Up to 8 million bbls/day; For unit of 175 m^3/hr 20.4 m^3 space & 9 tons weight	Compact modules satisfying all offshore applications; no chemical usage; reduction of TDS, dispersed oil and salt	No dissolved oil removal; fouling	This technology has been widely used for offshore produced water treatment; unstable flow rate caused by Harsh/Arctic Environment might reduce the efficiency
Centrifuge (Rye and Marcussen, 1993; Arthur *et al.*, 2005; Anlauf, 2007; Fakhru'l-Razi	Yes	No	Not Available (Higher than hydrocyclone)	Not Available	Lower than hydrocyclone	Higher efficiency than hydrocyclone; can remove smaller oil droplets in offshore produced water; low retention and high capacity	No dissolved oil removal; high maintenance and operational cost	Mainly on offshore gas platforms; unstable flow rate caused by Harsh/Arctic Environment might reduce the efficiency

et al., 2009; OSPAR, 2013)							
Flotation (Rubio *et al.*, 2002; Moosai and Dawe, 2003; Arthur *et al.*, 2005; Fakhru'l-Razi *et al.*, 2009; Igunnu and Chen, 2012; OSPAR, 2013)	Yes	A part of VOC (Benzene)	$1,568 ~$0	Satisfying all recent offshore produced water treatment facilities; For unit of 175 m^3/hr 75 m^3 space & 45 tons weight	High feasibility; can be easily integrated with other technology; easy operation, robust and durable	Low efficiency for toxic dissolved contaminants; Influenced by high-temperature; disposal of sludge	Frequently used in offshore oil and gas production; Since the temperature of produced water can be reduced rapidly, enhanced efficiency can be achieved, but less dissolved VOC might be removed; the strong ocean waves in harsh environments might also reduce the efficiency
Coalescence (Fakhru'l-Razi *et al.*, 2009; Igunnu and Chen, 2012) (Multon and Viraraghavan, 2006; Krebs *et al.*, 2013)	Yes	No	Not Available	Up to 260 m^3/hr (Mare's Tail); Up to 5,000 m^3/hr (Pect-F)	High feasibility; can improve efficiency of flotation, filtration, and other physical separation processes	No dissolved oil removal; chemical usage	Transportation and application of chemicals might be a problem in some cases
Filtration (integrated with coalescence) (Yao *et al.*, 1971; Liu *et al.*, 2005; Fakhru'l-Razi *et al.*, 2009; Igunnu and Chen, 2012; OSPAR, 2013)	Yes	No	Not Available	High (by paralleled units); For unit of 20 m^3/hr 0.16 m^3 space & 0.15 tons weight	High feasibility and high removal of TSS as well as oil and grease, low capacity requirement	Relative high retention, media regeneration required	Implemented on offshore platforms; The temperature might influence the energy consumption for feeding the water
Adsorption (Ranck *et al.*,	Yes	Yes	For unit of 15 m^3/hr,	For unit of 175 m^3/hr , the	High (by paralleled	Can remove dispersed and dissolved oil; compact modules;	High retention of water; chemical required for regeneration; high	Limited application on offshore platforms; high

2005; Jiuhui, 2008; Fakhru'l-Razi *et al.*, 2009; Igunnu and Chen, 2012; OSPAR, 2013)			cost is $50,000	operational cost can be $674,520/year	units); For unit of 6 m^3/hr 4.1 m^3 space & 1.9 tons weight		operational cost; reliability issue	retention and chemical application may raise some operational problems in Harsh/Arctic environments
Membranes (Bilstad and Espedal, 1996; Li *et al.*, 2006; Çakmakce *et al.*, 2008; Xu *et al.*, 2008; Fakhru'l-Razi *et al.*, 2009; Ebrahimi *et al.*, 2010; Igunnu and Chen, 2012; OSPAR, 2013)	Yes	Depends on type of membrane)	$167,000 (recent) $136,000 (new)	$1,223-5,641/kg aliphatic hydrocarbons	Low; For unit of 6 m^3/hr 20 m^3 space & 10 tons weight	Can remove dissolved salts, dispersed and dissolved oil; high efficiency on TSS and oil and grease removal and high water recovery	High cost and energy consumption; fouling; high weight and space consumption; low reliability on removal of dissolved small molecular contaminants (except reverse osmosis); pretreatment is required; high chemical loading may be required	Offshore application limits the regeneration, resulting in frequent system shut down and maintenance; compared to onshore applications, there are very limited offshore applications; the high chemical consumption might be problematic in harsh/Arctic environments; the low ambient temperature might reduce the concern of its operational temperature
Freeze-thaw evaporation (Thanasukarn *et al.*, 2006; Fakhru'l-Razi *et al.*, 2009)	Yes	Yes	Not available		Can be as high as possible	Removal of all dissolved contaminants; natural process; low energy consumption	Long operation cycle resulting in high retention of water	Has not been applied for offshore case because of its long retention; the low temperature in harsh/Arctic environments can shorten the operation cycle
Chemical oxidation (Morrow *et al.*, 1999; Fakhru'l-Razi *et al.*, 2009; Igunnu and Chen, 2012; Hong and Xiao, 2013; OSPAR, 2013)	Yes	Yes	$2350	$0.026/$m^3$ produced water	No maximum capacity; For unit of 350 m^3/hr 10.5 m^3 space & 5 tons weight	Removal of dissolved oils even at trace level; no chemical addition (UV/ozone); compact; easy operation; no chemical required; no feed water quality required; disinfection	Process monitoring and optimization are demanded; efficiency could be low with produced water's chemical species	Only in offshore trials; no specific challenge raised by this technology for harsh/Arctic environments application; its simplicity in operation might lead to convenience in unmanned operation which is preferred in such environments

2.4 Challenges in Harsh/Arctic Environments

Considerable offshore oilfields in harsh environments (mainly in a cold environment) such as the North Sea, the North Atlantic, and the offshore Alaska, have been developed during the last 60 years. Now, industrial activities are reaching locations in the Arctic and sub-Arctic regions due to the necessity of resource development (Bird *et al.*, 2008; Hamilton, 2011). Oil and gas development in the Arctic and sub-Arctic regions, which is in one of the harshest environments in the world, may need to face the challenges raised by its uniqueness including extreme and unpredictable climates, fragile biota, pollution persistence and lack of knowledge and data (Macdonald and Bewers, 1996; Reynolds and Tenhunen, 1996; AMAP, 2007; Khan *et al.*, 2015). Although oil spills have posed the largest threat to Arctic marine environments, other oil and gas operations, including produced water discharge, may also contribute to significant petroleum hydrocarbon inputs in the Arctic (Clarke and Harris, 2003). However, there are only a few recent studies directly dedicated to its environmental effects and related management.

2.4.1 Vulnerability of Harsh/Arctic Environments

In harsh environments, the ambient and water temperature can be very low. For instance, in the maritime zone of the Arctic, ocean temperatures range from 5—10 °C in the summer and 1—-1 °C in the winter (AMAP, 2007). The major concern caused by cold temperatures in the Arctic region is the slow recovery rate of the environment. Dilution, biodegradation, and vaporization are important mechanisms to reduce the concentrations of discharged hydrocarbons and other organic contaminants in the ocean. Dilution rates

may be lowered in cold water as produced water viscosity increases. Biodegradation and vaporization rates are typically reduced with decreased temperature. With slow natural contaminant reduction rates, contaminants tend to be more persistent in the receiving water and thus, chronic effects and exposures are magnified in harsh/Arctic regions. Additionally, contaminants that may have dissolved in warmer waters (such as produced water before discharge) might exist in a dispersed or less soluble state in cold waters. This mechanism dramatically affects their fate in the marine environment. The persistence of contaminants in the Arctic environment also increases the chances for organisms to be exposed to contamination. Animals such as seabirds are very sensitive to oil even in small concentrations. Seabirds and some marine mammals in cold regions depend on feathers or fur for insulation (O'Hara and Morandin, 2010). When their feathers/fur is fouled by dispersed oil including the fraction transformed from the dissolved fraction due to low temperature, they become very vulnerable to the cold, and in most of the cases, this leads to death.

Most of the polar ice pack forms in the upper layer of the ocean water where a thin membrane of tiny crystals initially forms on the surface. With the constant shifting of water, these crystals break up, adhere to other crystals, increase in size and eventually amalgamate to become a continuously moving sheet of ice (Spielhagen *et al.*, 2004). Most of the spring and summer melt occurs along marginal ice zones. Because of the open water associated with this region, a lot of biological activities also occur here (Clarke and Ackley, 1984). Ice on the surface of the water accumulates dispersed oil that rises to the water surface. Because marine mammals occupy the ice-air interface, this poses a significant danger. Ice will also prevent oil from mixing and being diluted and thus, oil (or contaminants) may concentrate

in one location, intensifying local impacts. Petroleum compounds that have less density than seawater will preferentially rise to the surface and be trapped under the ice and may partially melt the ice to form a slick that then spreads outward. The oil movement and the amount of trapped oil are functions of the under-ice surface roughness. Also, ice reduces the area of the water surface open for hydrocarbons to vaporize. Vaporization is an important mechanism that reduces concentrations of relatively toxic volatile aromatics (e.g., BTEX) in dissolved and dispersed oil in produced water. The discharge of contaminants in produced water with meltwater creates a hazardous environmental condition for ice-dependent fauna. If contaminated, these organisms may pass toxins on to higher trophic levels, such as marine fish and mammal populations, where they are readily stored in lipid material (Pfirman *et al.*, 1995). Sea ice also directly provides habitats for some fish species (e.g. polar cod, Arctic cod, saffron cod, and navaga) to lay eggs under the ice layer in winter. These eggs can be harmed by exposure to dispersed oil. Animals exposed to hydrocarbons in produced water may show the impact in some other locations and vice versa (O'Hara and Morandin, 2010; Burke *et al.*, 2012).

The animal gathering may also increase exposure time to contaminants. Moreover, similar to oil and gas operations in other regions, seabirds, and fish are attracted by offshore structures leading to extended exposure time to pollutants. During their aggregation, animals tend to be more vulnerable to environmental hazards because they are typically in their sensitive period such as during spawning. Aquatic animals are most sensitive to exposure to oil contaminants in their larval stages. Significant variations in population sizes from year to year also result in difficulty (or impossibility) in evaluating population-level effects that are solely contributed by hydrocarbon discharge.

The harsh/Arctic area also has long seasonal changes where extended periods of darkness and cold in winter, and sunlight in summer, occur. This weather condition creates unique characteristics of Arctic ecosystems. The short spring and summer are the only time of productivity during a year. This period is the time when animals migrate around the world and tend to aggregate in specific areas at high productivity. Seasonal changes lead to variations in the habitats of Arctic animals and their migration/aggregation patterns. These cause complexity and difficulties in assessing the impacts of produced water discharge in the Arctic environment. Furthermore, lack of sunlight results in a low photochemical degradation rate of organic compounds. Highly and semi-volatile organic compounds such as two and three-membered-ring PAHs are transported over long distances during the summer. The falling snow was also found to be an efficient "scavenger" of volatile compounds and particulates, bringing contaminants in the atmosphere into the water (Macdonald *et al.*, 2003).

There are relatively few species in the Arctic ecosystem. The food chains are simple and vulnerable to contaminants in produced water (Kelly and Gobas, 2003; Wolkers *et al.*, 2004). With such low biodiversity and simple food webs, disturbance by hydrocarbons to one species can affect the entire food chain. For example, releasing oil containing produced water in spawning areas could significantly reduce the year's new population of the specific species. This consequence may cause severe effects on higher-level animals of the food chain, resulting in food deficiency or cascading toxicity impacts.

PAHs can be categorized as Persistent Organic Pollutants (POPs) (Henner *et al.*, 1997). Ultraviolet light (from the sun) and PAHs absorbed by some animals, especially translucent and shallow-water animals, can interact and result in "many times more toxic" effects than

from each of them alone (Hatch and Burton, 1999; Echeveste *et al.*, 2011). The decreasing levels of ozone in the stratosphere over the North Pole can also intensify this problem.

2.4.2 Implications for Produced Water Management

Due to the vulnerability of ecosystems, oil and gas projects are often subject to a "zero–discharge" schemes; for instance, in Norway (Knol, 2011), and at BP's Northstar oil field in the North Slope Alaska (Inc., 2012). At the Northstar oil field, a single well is drilled and used for disposal to achieve zero waste discharge. In the Norwegian Barents Sea (with approximately 400 m water depth), no new oil and gas development is permitted without "zero discharge" due to environmental concerns. For existing licenses, produced water reinjection is required. Discharge of the maximum of 5% fully treated produced water is allowed during injection equipment downtime (Pinturier *et al.*, 2008; Buffagni *et al.*, 2010). These facts indicate that more stringent policies are currently applied in harsh/Arctic environments due to the increased vulnerability, and these policies might be expanded and developed as mature regulatory systems targets harsh/Arctic environments in the future.

In the Arctic or other cold climates, contaminants in produced water that were previously ignored due to low concentrations and high dilution rates may become a concern due to the possible low dilution rates, ice cover, etc. Therefore, management systems may need to be improved to be capable of removing these contaminants before discharge or injection. In most water treatment systems, water viscosity plays a vital role in the performance of treatment units, in particular for those relying on gravity separation technologies. The viscosity of the fluid increases with reduced temperature. In cold climates, the increasing viscosity of oil droplets decreases as water viscosity increases; thus,

the smallest size range of oil droplets can be removed by treatment units may be reduced. On the other hand, compounds that can be volatilized in warmer climates may stay in the dissolved phase, and therefore, are not removed before discharge. These compounds, such as BTEX, typically have high toxicity, leading to adverse effects on ecosystems if released without effective treatment. However, at low temperatures, produced water components tend to have reduced water solubility, thus staying in the dispersed oil phase. This mechanism may be beneficial from a treatment point of view because conventional treatment systems can remove the formed dispersed oil.

Oil removal efficiency in most produced water treatment units is reduced when they experience high fluxes in influent, especially those with short retention times such as hydrocyclones. In harsh offshore environments, wave motions can cause inconsistent flow rates. Motion or vibration may also result in mechanical problems in systems with moving parts or systems that rely on smooth water surfaces. This condition limits applications of some traditional treatment technologies. For example, the flotation method utilizes skimming paddles to skim off oil foam from the water surface. Without a stable water surface, the desired oil removal efficiency may not be achieved.

In extreme climates where manned operational controls are limited, managements usually require highly reliable technologies, which are insensitive to motion and highly automated, require low maintenance, low chemical, and low energy consumption. Because of the lower level of control and discharge monitoring, low down-time equipment is needed. Preventive measures such as frequent inspections (as many as possible) for leaks or mechanical problems and sound treatment/management strategies may be necessary to avoid accidental spills. This requirement can be crucial given the expanding exploration

and development activities in the Arctic area. On the other hand, this environment poses additional risks to the choice of treatment/disposal options, including accidents and produced water spills. Environmental risk assessments or environmental effects monitoring for oil and gas production projects, though crucial for the vulnerable Arctic ecosystems, are difficult to conduct and maintain.

2.5 Advanced Oxidation Technologies

The most widely used advanced oxidation technologies are UV irradiation and ozonation. The kinetics of direct photolysis of organic pollutants in cleaner water have been widely studied (Beltran *et al.*, 1993; Beltrán *et al.*, 1996; Lehto *et al.*, 2000; Ledakowicz *et al.*, 2001; Miller and Olejnik, 2001; Fasnacht and Blough, 2002). According to their results, light screening effect is a major factor for degradation of PAHs. In natural water or wastewater, more complicated chemical constituents can lead to various unidentified kinetics, resulting in difficulties to conduct numerical simulation (Shemer and Linden, 2007; Jasper and Sedlak, 2013; Jing *et al.*, 2014a).

Ozone is a highly powerful oxidant that can attack organic materials and convert them to nonhazardous products. Ozonation is a technology that has already been successfully applied to the treatment of drinking water or municiple wastewater (Wang *et al.*, 2003; Hollender *et al.*, 2009; Rakness, 2011; Stalter *et al.*, 2011; Xu *et al.*, 2012; Antonopoulou *et al.*, 2014) and industrial wastewater effluents (Lin *et al.*, 2014; Rubio-Clemente *et al.*, 2014; Wu *et al.*, 2015). It was reported that ozonation could decompose the dissolved

organic compounds (Morrow *et al.*, 1999). Volatile hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX) were effectively removed from the salty water when small bubbles of O_3 gas were generated by electrostatic spraying or a small-pore bubble diffuser (Walker *et al.*, 2001). Their experiment showed extractable organics could be destroyed after three-day ozonation. These studies also indicated that the destruction of soluble organics using ozonation alone may be costly as it requires large contact vessels and long contact times (Martin *et al.*, 2010; Cheng *et al.*, 2011; Igunnu and Chen, 2012; Pereira *et al.*, 2013). Pereira et al. suggested that ozonation might present great potential for decomposing dissolved organic compounds in onshore produced water during oil sands process. Combined with other methods (e.g., photocatalytic oxidation, biological remediation, and flocculation), ozonation might be a more viable option for the cost-effective treatment of offshore produced water. However, there were limited studies known in the literature, and they focused on removal of PAHs, considering the influencing factors and matrix effect of produced water (Wang *et al.*, 2013). Moreover, the impact of ozonation on the toxicity and biodegradability of produced water is unknown.

Ozone is an important oxidant in nature, and it is the precursor to transient secondary oxidant species via reactive decomposition in aqueous solutions. Molecular ozone has a higher oxidation potential of 2.07 V than conventional chemical oxidants such as potassium permanganate and chlorine (Ikehata and Gamal El-Din, 2005b). It has been known that ozone reacts with aromatic compounds to give either substitution (atom attack) or ring-opening (bond attack) (Russo *et al.*, 2010). For instance, the reactivity of PAHs to ozone is correlated with the atom or bond localization energies of the compounds (Perraudin *et al.*, 2007b). The smaller the localization energy, the greater is the reactivity of the bond at

a certain position of the aromatic ring (Naddeo *et al.*, 2011).

Ozonation is a process of infusing water with ozone, which has been widely used in water/wastewater treatment to facilitate the breakdown of organic pollutants. In some cases, it is regarded as an AOP because of decomposition of ozone molecules into hydroxyl radicals through the chain reaction. The reactions between the radicals and organic molecules would, therefore, occur (Ikehata and Gamal El-Din, 2005a). Hydroxyl radical has a higher oxidation potential (2.8 V) than the molecular ozone. It can attack organic and inorganic molecules non-selectively with high reaction rates.

Chemical reactions involved in ozone oxidation processes can be divided into two categories: direct oxidation and indirect oxidation (Chu and Ma, 2000; Ikehata and El-Din, 2004), depending on the reaction conditions such as pH. In the first category, the oxidation of the targeted compounds is carried out by the parent oxidizer: ozone. The typical modes of attack involve the insertion of the ozone molecule into unsaturated carbon-carbon bonds which results in the formation of an ozonide. Indirect pathway is largely based on hydroxyl radical (OH·) attack to induce the oxidation of the contaminants. Hydroxyl radicals are nonselective oxidizers, which can rapidly attack organic contaminants and break down their carbon-carbon bonds. In the aqueous phase, the oxidation pathway is mainly affected by pH, where direct ozonation favors low pH while hydroxyl radical's formation is achieved at high pH (Haapea and Tuhkanen, 2006). At low pH, molecular ozone reactions are predominant where organic compounds are subjected to the electrophilic attack of ozone molecules and decomposed into carboxylic acids as final products. The molecular ozone reactions are selective to the organic molecules having nucleophilic moieties such as carbon-carbon double bonds, -OH, $-CH_3$, $-OCH_3$, and other nitrogen, oxygen, phosphorus,

and sulfur bearing functional groups (Alvares *et al.*, 2001). It is also known that aromatic compounds are selectively decompose through ozonolysis. On the other hand, in the presence of hydroxyl anion (HO^-), ozone molecules are decomposed into free radicals ($\cdot O_2^-$ and $HO_2\cdot$), and subsequently produces hydroxyl radical ($HO\cdot$), which will attack organic compounds. The radical reactions are nonselective and powerful chain reactions, which can convert organic compounds to the ultimate mineralization. The complete sets of radical reactions can be found in the literature (Wang *et al.*, 2003). Generally, PAH-ozonation in aqueous media can take place by both direct and radical reactions at neutral pH (Kornmüller and Wiesmann, 2003).

Research showed that direct oxidation of ozonation is exclusive to the organic molecules having nucleophilic moieties, such as carbon-carbon double bonds, aromatic rings, and the functional groups bearing sulfur, phosphorus, nitrogen and oxygen atoms. Contrastingly, hydroxyl radical reactions are non-selective toward various organic and inorganic compounds through hydrogen abstraction, radical-radical reactions, electrophilic addition, electron transfer reactions, and eventually, lead to the complete mineralization of organic compounds (Oppenländer, 2003; Ikehata *et al.*, 2006).

During the treatment by ozonation, organic pollutants such as PAHs and BTEX undergo a series of oxidation and spontaneous transformation reactions. In other words, primary degradation products are often subject to further degradation. The disappearance of parent compounds does not always indicate successful treatment because the degraded products may be as biologically active (or toxic) as the parent compounds. Therefore, it is desirable to assess the residual toxicity or estrogenicity after the treatment to ensure the safety of treated wastewater or water (Ikehata *et al.*, 2008).

Some of the advantages of ozonation include the complete mineralization of organic contaminants, the production of less harmful and more biodegradable by-products, and the ability to handle fluctuating flow rates and compositions (Zhou and Smith, 2002).

The reaction rate of PAHs during ozonation in aqueous phase can be described by the following equation (Kornmüller and Wiesmann, 2003)

$$-\frac{dC_{PAH}}{dt} = k_{O_3} C_{PAH}^{n} C_{O_3}^{m} + k_{OH} C_{PAH}^{n} C_{OH}^{m}$$

Where n and m are reaction orders, k_{O3} is the reaction rate constant of direct reaction, k_{OH} the reaction rate constant of the radical reaction, C_{PAH} the PAH-concentration, C_{O3} the dissolved molecular ozone concentration and C_{OH} the concentration of radicals.

Commonly in water solutions, second-order kinetics can better describe the reactions (Beltrán *et al.*, 1999; Von Gunten, 2003a). For the highly-condensed PAHs in oil/water emulsions, selective ozonation could be described micro-kinetically by a direct ozone reaction of pseudo-first order (regarding PAHs concentrations). The mean reaction rate constant of PAHs is about 1.02 min^{-1} in oil/water emulsions and is in the upper range as compared to those achieved for PAHs dissolved in water (Kornmüller and Wiesmann, 2003). Even in the case of PAHs adsorbed on a solid matrix (silica particles), the decay of particulate PAH concentrations versus time follows a pseudo-first order kinetic (Perraudin *et al.*, 2007a, 2007b).

However, most of the reaction constants reported in the literature refer to both reaction types ($k = k_{O3} + k_{OH}$) (Kornmüller and Wiesmann, 2003). Russo et al. summarized the kinetic constant k for the degradation of different PAHs by ozone (Russo *et al.*, 2010).

Ozonation is a technology that has already been successfully applied to the treatment

of industrial wastewater effluents from various industries (Lin *et al.*, 2014; Rubio-Clemente *et al.*, 2014; Wu *et al.*, 2015). It was proposed that ozonolysis can decompose the dissolved organic compounds (Morrow *et al.*, 1999; Pereira *et al.*, 2013). Experiments of ozonation treatment of phenanthrene in aqueous solutions showed that oxidation proceeded mostly with molecular ozone at neutral pH (Trapido *et al.*, 1994). Dissolved BTEX, which are constituents of produced water, could also be effectively removed from the salty water when small bubbles of O_3 gas were generated by electrostatic spraying or a small-pore bubble diffuser (Walker *et al.*, 2001). Klasson et al. compared the destruction of soluble organics in synthetic and real produced water by sonochemical oxidation and ozone (Klasson *et al.*, 2002). Sonochemical oxidation could destroy some compounds such as BTEX. Their experiments showed that nearly all extractable organics could be destroyed after three-day exposure to ozone. These studies indicate that the destruction of soluble organics using ozonation alone may be costly as it requires long contact time.

Combined with other methods (e.g., sand filtration, UV irradiation, photocatalytic oxidation), ozonation can be a viable option for the cost-effective treatment of produced water. A new ozonation technique coupled with sand filtration has been developed to quickly remove oil from process water and prevent oil sheen (Cha *et al.*, 2010). Kwon et al. studied the degradation of lowly concentrated phenanthrene and pyrene in the aspect of kinetics under UV irradiation (Kwon *et al.*, 2009). The results suggested an inverse relation between the reaction constants and the number of molecules due to agglomeration of hydrophobic molecules in the aqueous environment. Wang et al. studied the decomposition of two halo-acetic acids using UV and ozone as well as their combinations including UV/ozone, UV/H_2O_2, ozone/H_2O_2, and UV/ozone/H_2O_2 (Wang *et al.*, 2009). They argued

that single UV or ozone does not result in perceptible decomposition of target organics. Kishimoto and Nakamura investigated the effects of ozone bubble size and pH on the efficacy of UV/ozone treatment. The results indicated that increase in bubble size and the decrease in pH resulted in higher ozone utilization efficiency (Kishimoto and Nakamura, 2011). They argued that this enhancement of ozone utilization was attributed to the shift of the production pathway of OH from O_3^- to the UV photolysis of H_2O_2. The degradation of FLU, phenanthrene, and acenaphthene applying O_3/UV was studied by Beltran et al. (Beltran *et al.*, 1995). The influence of hydroxyl radical inhibitors and pH on the reaction solution were investigated. The most important pathways of PAHs oxidation, except for FLU, are the direct ozonation and photolysis. The combination of ozone with UV radiation leads to a slight increase in the oxidation rate of PAHs as compared to the results obtained from the ozonation or photolysis alone. Tehrani-Bagha et al. applied UV-enhanced ozonation processes to the degradation of two organic surfactants and confirmed that the synergistic effects of ozone and UV were more effective than the individual processes (Tehrani-Bagha *et al.*, 2012). Lucas et al. further examined the effectiveness of ozone, UV/ozone, and UV/ozone/H_2O_2 on the treatment of winery wastewater in a pilot-scale bubble column reactor (Lucas *et al.*, 2010). Analysis of the experimental data demonstrated that UV/ozone/H_2O_2 has the highest efficiency, followed by UV/ozone and ozone at the neutral pH. Aliaga et al. reported the removal of organic capping agents from Platinum colloid nanoparticles using UV/ozone treatment (Aliaga *et al.*, 2009). Significant reduction of oil and grease and other contaminants in petroleum refinery water was reported using a heterogeneous system of O_3/TiO_2/UV followed by contact with macroalgae (Corrêa *et al.*, 2009).

2.6 Summary

Since the discharge of large amounts of produced water is usually required for offshore oil and gas production, the dispersed and dissolved contaminants in produced water are of great environmental concern. However, produced water toxicities and risks of produced water in cold regions have been sparely studied. As the vulnerability of harsh/Arctic environments can significantly increase the environmental impact, studies to understand those increased toxicological effects, changed contaminant fate, and transformed mechanisms, are of crucially demanded. On the other hand, in such vulnerable environments, more than 95% of offshore produced water is usually required to be reinjected due to difficulties in monitoring, treatment and impact assessment. This strategy can be costly and highly limited by the well-injectivity. Additionally, organic pollutants in produced water are typically measured as oil and grease which ignores the contributions of individual contaminants such as highly toxic PAHs and APs. Therefore, although more stringent policies are applied to typical oil fields in harsh/Arctic environments, there is still a need for developing more consumate and mature regulative systems to satisfy the increased oil and gas production development in harsh/Arctic environments. Both produced water re-injection and disposal require the application of particular treatment technologies. Present offshore treatment technologies are focusing on removal of dispersed contaminants. Dissolved contaminants, however, remain in the discharged water leading to some significant environmental impacts due to the increased vulnerability of the environment.

The efficiency and feasibility of emerging technologies are either influenced by offshore operational limitations or challenges inharsh/Arctic environments. This situation translates into the demand for more advanced technology tackling the challenges of offshore produced water management in harsh/Arctic environments. AOPs as the promising technologies to fill this gap, there are limited study to investigate the UV irradiation and ozonation process for offshore produced water, the affected performance and complicated mechanisms and kinetics by offshore produced water substrate are still unknown. Therefore, there is a need for such research to fulfill these questions.`

CHAPTER 3 DEVELOPMENT OF DETERMINATION METHODS FOR 16 PAHS IN OFFSHORE PRODUCED WATER ANALYSIS

The contents of this chapter are based and expanded on the following paper:

Jisi Zheng, Bo Liu, Jing Ping, Bing Chen, Hongjing Wu, Baiyu Zhang: *Vortex- and Shaker-Assisted Liquid–Liquid Microextraction (VSA-LLME) Coupled with Gas Chromatography and Mass Spectrometry (GC-MS) for Analysis of 16 Polycyclic Aromatic Hydrocarbons (PAHs) in Offshore Produced Water*. Water Air and Soil Pollution 09/2015; 226(9). DOI:10.1007/s11270-015-2575-3

Role: Jisi Zheng did most experimental work under Dr. Bing Chen and Dr. Baiyu Zhang's supervision. Bo Liu and Dr. Jing Ping provided considerable assistance in the lab work. Dr. Hongjing Wu aided in DOE analysis of the results. Dr. Baiyu Zhang also provided considerable advices for drafting the paper.

3.1 Background

Polycyclic aromatic hydrocarbons (PAHs) are the petroleum hydrocarbons with the greatest environmental concern in produced water because of their well-known toxicity and persistence in the marine environment (Manoli and Samara, 1999). Since PAHs naturally exist in crude oil (Dórea *et al.*, 2007) environmental issues can be raised when PAHs enter the eco-system by discharging produced water that is not adequately treated (Fakhru'l-Razi *et al.*, 2009; Igunnu and Chen, 2012). Since produced water counts for the largest waste stream from oil and gas industry (Clark and Veil, 2009), the economical and efficient monitoring of the PAH concentrations in produced water implies a great significance to the stakeholders for waste management.

The conventional pre-treatment techniques for PAH analysis in water such as liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are time, sample and solvent consuming (Titato and Lanças, 2006; Dórea *et al.*, 2007). To overcome these drawbacks, a solid-phase microextraction (SPME) was developed by Arthur and Pawliszn in 1990 (Arthur and Pawliszyn, 1990). However, despite its solvent-free character, SPME's low recommended injection and operating temperature (240–280 ^{o}C), high expense and the risk of fiber breakage significantly limit its applications (Dietz *et al.*, 2006). Recently, liquid-phase microextraction (LPME) such as single drop microextraction (SDME), hollow fiber liquid-phase microextraction (HF-LPME) and solvent bar microextraction (SBME) have been widely used for sample pre-treatment. These techniques have excellent sensitivity and consume less solvent (Sarafraz-Yazdi and Amiri, 2010). An SDME method followed by high-performance liquid chromatography (HPLC) with a high efficiency and an excellent

sensitivity in wastewater was carried out by Wu et al. (Yunli Wu *et al.*, 2008). However, the complex instrumentation and procedure, as well as the high requirements for the lab skill, lead to the difficulties in the operation and automated injection with commercial auto-samplers. The developed methods based on HF-LPME and SDME are still inheriting their limitations such as a higher cost (Popp *et al.*, 2001; Charalabaki *et al.*, 2005).

Rezaee et al. developed a more rapid and low-cost method named as dispersive liquid-liquid microextraction (DLLME). Ultrasound energy was then introduced to extract PAHs and other compounds to reduce the usage of solvents (Song *et al.*, 2011; Donthuan *et al.*, 2014). Ozcan et al. carried out a study using ultrasound assisted dispersive liquid-liquid microextraction (UA-DLLME) followed by GC-MS analysis (Ozcan *et al.*, 2010). This improvement provided a more simple and efficient DLLME method with less solvent usage for detection of 16 PAHs in environmental samples including wastewater. However, the transmission of ultrasound energy in the samples can potentially cause degradation of analytes during the extraction, leading to the reduction of accuracy (Psillakis *et al.*, 2004; De Castro and Priego-Capote, 2007; Sanchez-Prado *et al.*, 2008).

LLME technique such as vortex-assisted liquid-liquid microextraction (VA-LLME) and up-and-down shaker-assisted liquid-liquid microextraction (UD-SA-LLME) was developed by Yantzi et al. and Wang et al. in 2010 and 2014 (Yiantzi *et al.*, 2010; Zacharis *et al.*, 2012; Ku *et al.*, 2013), respectively. These techniques were used with simplified procedures, lowered toxic solvent consumption, and lower cost. The vortex can produce dispersive solvent cloud to increase the interfacial surface while the shaking can keep the solvent dispersed in the tube to reduce the gradient distance. Both methods were approved to have good performance when detecting trace level of PAHs in wastewater without the

usage of dispersion solvents. However, only the manually injection was adopted in these studies. For intensive detection in offshore platforms, the automated injection using auto-samplers of a GC-MS are preferred. Moreover, till now, no study was conducted to integrate vortex and shaker to improve the performance of LLME treatment.

Although several studies have been carried out to analyze 16 PAHs by applying different analytical techniques in various water sample matrices (Pino *et al.*, 2002; Delgado *et al.*, 2004; Dórea *et al.*, 2007; Saraji and Boroujeni, 2014), rare studies were focusing on PAHs in samples that have both high salinity and high organic content (e.g., offshore produced water). The objective of this study is thus to develop a rapid, simple, low-expense, low-toxic and efficient analytical method capable of intensive detection of PAHs in offshore produced water. The United States Environmental Protection Agency (U.S.EPA) has recommended 16 PAHs as priority pollutants (Yan *et al.*, 2004). These PAHs are most representatives and thus selected as the target PAHs in this study. For the first time, the pretreatment method namely vortex and shaker assisted liquid-liquid microextraction (VSA-LLME) was developed and coupled with GC-MS for analysis of 16 PAHs in offshore produced water. Both one-factor-a-time (OFAT) and design of experiment (DOE) optimizations were conducted for enhancing the method performance.

3.2 Methodology

3.2.1 Standards, reagents, apparatus and produced water samples

The 16 PAH standard mix was supplied by Agilent® Technologies Inc. (p/n 8500-6035). The PAH stock solution had a nominal concentration of 500 µg/ml naphthalene (NAP); acenaphthylene (ACY); acenaphthene (ACE); fluorine (FLO); phenanthrene (PHE); anthracene (ANT); fluoranthene (FLA); pyrene (PYR); chrysene (CHR); benz[a]anthracene (BaA); benzo[b]fluoranthene (BbF); benzo[k]fluoranthene(BkF); benzo[a]pyrene (BaP); dibenz(a,h)anthracene (DahA); indeno(1,2,3-cd)pyrene (IcdP); benzo[ghi]perylene (BghiP). The ultra-high purity water and solvents including dichloromethane and acetone of reagent grade or equivalent quality were purchased from VWR® International (Mississauga, Ontario, Canada) and Fisher Scientific (Ottawa, Ontario, Canada). The Kimble Chase disposable plain 10 ml glass centrifuge tubes were used to contain the samples and extraction solvents throughout the extraction. GC supplies, including deactivated single tapered glass inlet liners and J&W Scientific DB-5MS UI fused silica capillary columns, were obtained from Agilent® Technologies Inc. (Mississauga, Ontario, Canada).

The offshore produced water samples were collected from an offshore oil and gas platform. Right after the collection from the sampling port, the samples were bottled in an acid washed Nalgene® 10L high-density polyethylene (HDPE) jerrican and then placed in a cooler. Ice packs were applied to cool down the produced water samples immediately. The ice packs could also help to maintain the low temperature and keep the regular position to avoid swash of produced water. When entering the lab, the produced water samples were

placed in a 4 oC fridge and the darkness condition inside fridge was adopted to avoid light radiation to the samples. The collected produced water samples have high salinity and organic loading. The pH, salinity and chemical oxygen demand (COD) of the sample were 6.88, 41.94 ppt and 3154 ppm, respectively. Also, 16 PAHs expect NAP were all below the limits of detection (LODs) of the method, so the samples were also spiked to test the recovery of the method.

3.2.2 Vortex and Shaker Assisted Liquid-liquid Microextraction

Extraction Solvent

The properties of an extraction solvent are very important for achieving well performed VSA-LLME. In traditional LLME, the extraction solvent must be denser than water to allow separation by centrifuge after the extraction. It also should be insoluble in water to achieve high enrichment factor (EF). Therefore, the halogenated compounds such as chloroform, tetrachloride carbon and chlorobenzene are widely used for this purpose. However, these solvents have high toxicity and may raise safety issues. The dichloromethane is a less toxic chlorinated hydrocarbons, and its density (1.3266 g/cm^3) is greater than the density of water. It is also a frequently used solvent with less cost and good availability. Therefore, the dichloromethane was used as the extraction solvent in the study.

Optimization of Operation Parameters

Parameters for VSA-LLME treatment including the volume of the extraction solvent, extraction time, ion strength and centrifuge speed were optimized. Three levels of extraction solvent volume (250 μL, 500 μL, and 1000 μL) were selected for the one-factor-

a-time (OFAT) optimization. When the solvent volume was less than 250 µL, the volume of the organic phase was less than 100 µL, causing an observed difficulty in transferring extractant effectively to the micro-vial. The EF was used as the response of the OFAT treatment.

Comparing to the traditional OFAT method, the statistical design of experiment (DOE) method can optimize the set of experiments by providing more information per trial and examine the interactions of different factors (Wu *et al.*, 2012). The DOE method was applied to investigate the effects of ionic strength, shaking time and centrifuge speed on VSA-LLME performance. The interactions among the parameters were also explored. The average extraction yields (EYs) of 16 PAHs were selected as the response of the DOE model. Total eight runs were conducted based on the two-level factorial design for three factors (**Table 3.1**). Design Expert ® was used to analyzing the effects of main factors and their interactions. The lower level of NaCl was set to 0.5 g since the salinity of the produced water samples is around or above 50 parts per thousand (Clark and Veil, 2009; Fakhru'l-Razi *et al.*, 2009). The EF and EY were quantified using the mathematical equations in below:

$$EF = \frac{C_{org}}{C_{aq}} \qquad (1)$$

$$EY = C_{org} \times S + I = ER\% \times C_{aq} \times \frac{V_{aq}}{V_{org}} \times \frac{S}{100} + I \qquad (2)$$

Where C_{org} (µg/L) is the determined concentration in organic phase; C_{aq} (µg/L) is the initially spiked concentration in aqueous phase; V_{org} (µL) is the volume of a water sample;

V_{aq} (μL)is the residual solvent after extraction; S is the constant for slope of the calibration curve; I is the intercept of the calibration curve; ER% is the extraction recovery for an analyte.

VSA-LLME Procedures

As shown in **Figure 3.1**, a 10 mL water sample was transferred into a 10 mL glass centrifuge tube. The dichloromethane was then added to the sample as the extracting solvent. The mixture was then placed on a vortex mixer for 10 s at 3000 rpm to form fine droplets cloud. The mixture of sample and solvent cloud was transferred into a holder on the shaker. The intensity was set to 1000 to keep the droplets dispersed in the sample. After shaking, the emulsion of the mixture was centrifuged for 5 min to achieve the phase separation. After that, 50 μL of the organic phase was extracted from the bottom of the tube using a 100 μL Agilent syringe (Agilent Technologies Inc.) and transferred into a 150 μL micro vial with a 2 ml GC vial outside (Agilent Technologies Inc.). The GC vial was then placed on the tray of the auto-sampler for GC-MS analysis. The vortex agitator was Corning® LSE™ Vortex Mixer. The shaker used for extraction was VWR® Incubating Mini Shaker. The emulsion of the mixture was centrifuged with a VWR Clinical 200 Large Capacity Centrifuge (VWR, Canada).

The volume of dichloromethane, the extraction time using shaking, and the centrifuge speed were determined based on the optimization results.

Table 3.1 Experiment settings

Run	A: NaCl (g)	B: Shaking time (min)	C: Centrifuge speed (rpm)	EY
1	1	15	1000	10.818
2	0.5	15	1000	11.32
3	0.5	15	3000	10.113
4	0.5	5	1000	9.523
5	1	5	3000	9.428
6	1	5	1000	9.584
7	0.5	5	3000	10.848
8	1	15	3000	9.023

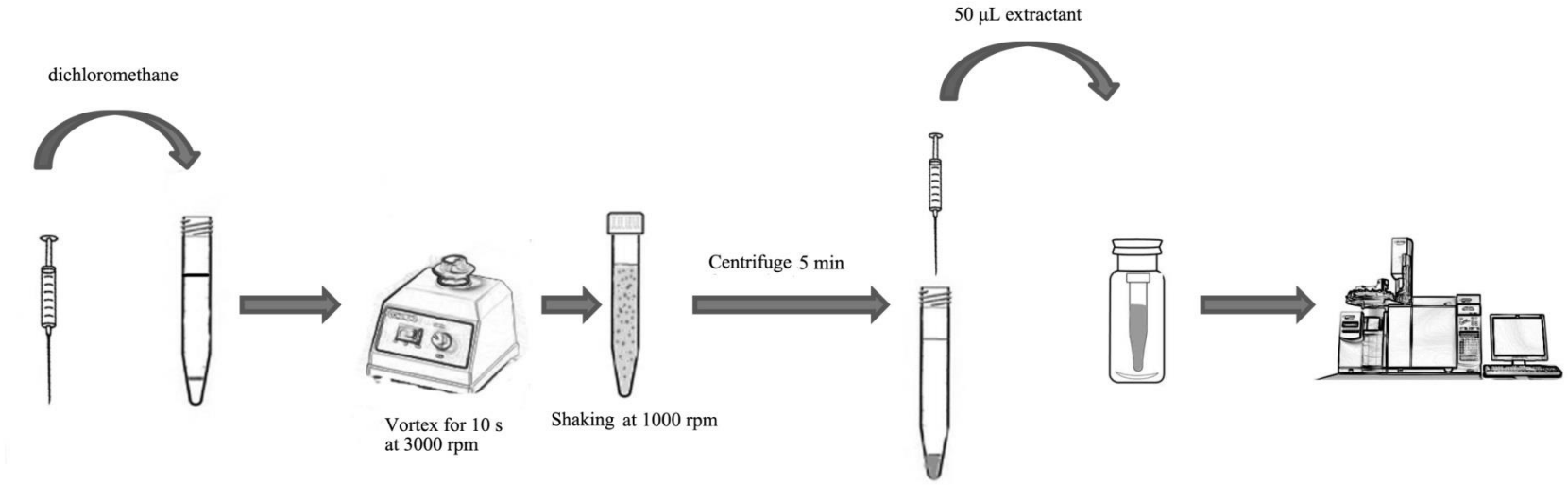


Figure 3.1 Extraction procedure in VSA-LLME treatment

Instrumentation

PAH analysis was performed using an Agilent 7890A/5975C GC-MS system equipped with an Agilent 7693 auto-sampler. Data acquisition, processing, and evaluation were carried out using Agilent ChemStation® software Version 2.01. The 16 PAHs were identified by mass spectrum using the NIST/EPA/NIH Mass Spectro Library Version 2.0f. The analytes were separated on a 30 m × 0.25 mm id × 0.25μm DB-5MS UI fused silica capillary column. An electronic pressure control was utilized to maintain a constant carrier gas (Helium of ultra-high purity) flow of 1.5 mL/min throughout the oven program. Sample injections (2μL) were performed using a split/splitless injector (single tapered inlet liner) in splitless mode at 300 °C. The transfer line temperature from the GC to the ion source was 300 °C. PAH analyses were performed by the electron impact ionization (EI) in both full scan and SIM mode. The initial temperature of the oven was 60 ºC, and then the temperature was raised to 300 ºC at 4 ºC/minute. A single run lasted 60 minutes.

The high resolution was achieved among the pairs of PAHs that have the same primary ion and close retention times (**Table 3.2**), and the sensitivity was thus enhanced. The main ions monitored for quantification and qualification were shown in **Table 3.2**. A higher ion-source temperature (350 ºC) was applied, and the significant elimination of tailing peaks was achieved especially for PAHs with more than four rings. Seven calibration standards with multiple spiked concentration levels were prepared by diluting the stock in dichloromethane. The calibration range was between 0.01 and 20 ng/ml. **Table 3.2** indicated that the instrumental setting provided an excellent sensitivity and thus led to a good linearity ($R^2 > 0.998$) during GC-MS calibration. The analytical performance of the optimized VSA-DLLME coupled with GC-MS was evaluated by measuring the linearity,

EFs, limits of detection (LODs), recoveries (RR%) and relative standard deviation (RSD%).

3.3 Results and Discussion

3.3.1 Enhancement of GC/MS analysis

The sensitivity of GC/MS is highly related to factors such as peak shape, resolution, and abundance. In previous enhancement process, the peak shape was optimized by solvent selection. Therefore, the GC/MS analysis was only tested and enhanced majorly targeting on the resolution and peak abundance.

Temperature ramp adjustment

Resolution is a critical factor when analyzing the compounds with chromatographic techniques. It is directly determining the resolution and instrumental analytical efficiency. In GC/MS analysis, the quantitation does not need high resolution between peaks in the case of that the quantitation ions of target compounds with similar retention time are different. However, for the determination of 16 PAHs, 4 pairs of PAHs have similar retention time and the same primary ion (PHE and ANT; CHR and BaA; BbF and BkF; DahA and IcdP). This problem sometimes could be solved by using less abundant ion that does not occur in the other compound's mass spectrum as quantitation ion. However, this change will reduce the peak abundance as well, and for most pairs, the three largest ions were the same. Therefore, to maintain low enrichment factor and low calibration range, the primary ions were still selected in quantitation, so good resolutions were still required for

those peaks in each pair for maintaining high sensitivity. For achieving good resolutions, three scenarios of temperature ramp (**Table 3.3**) were tested for PAHs in DCM.

Scenario 1 was derived from U.S.EPA standard method. As shown in **Figure 3.2** (b), since the resolution between BbF and BkF was relatively low, the adjustment of temperature ramp was needed. Therefore, Scenario 2 was developed by finer adjustment to achieve higher resolution and shorter time. The comparisons between scenario 1 and 2 are also shown in **Figure 3.2** (a) and (b). The total run time of scenario 2 was shortened to approximate 30 minutes and the resolution between BbF and BkF was enhanced as well as the peak abundance of large PAHs. However, the resolution between IcdP and DahA was still low. For solving this problem, a longer temperature ramp (Scenario 3) was tested. The results are shown in **Figure 3.3**. Though the resolution of the last pair was improved, the resolutions of the other pairs were reduced again since longer temperature ramp increased the peak tailings. The tailing of the peaks could be the major reason that the resolution was reduced by increasing the separation time. Thus, further improvement was focusing on the adjustment of ion-source temperature which may not only reduce the tailings but also can enhance the abundance.

Table 3.2 GC-MS calibration using PAH standards

	Ions monitored for quantization	(m/z)	Ions monitored for confirmation	(m/z)	Retention time (60 min)	Calibration Range[a] (ng/ml)	Linearity (R^2)
NAP	128		127,129		11.26	0.1~20	0.9996
ACY	152		151		19.55	0.1~20	0.9999
ACE	153		154		20.56	0.1~20	0.9999
FLO	165		166		23.53	0.1~20	0.9999
PHE	178		176		28.91	0.1~20	0.9998
ANT	178		176		29.2	0.1~20	0.9997
FLA	202		200		35.74	0.1~20	0.9998
PYR	202		200		36.92	0.1~20	0.9998
CHR	228		226		44.01	0.1~20	0.9986
BaA	228		226		44.19	0.1~20	0.9985
BbF	252		250,253		49.79	0.1~20	0.9987
BkF	252		250,253		49.93	0.1~20	0.9962
BaP	252		250,253		51.3	0.1~20	0.9985
DahA	276		277,274		56.35	0.1~20	0.9993
IcdP	278		274		56.62	0.1~20	0.9984
BghiP	276		274,277		57.35	0.1~20	0.9981

[a]8-point calibration (0.1, 0.2, 0.5, 1, 2, 5, 10, 20 ng/ml)

Table 3.3 Scenarios of temperature ramp

	Oven temperature ramp	Ion source temperatures
Scenario 1[d]	45 min multiple ramp [a]	230 °C
Scenario 2	33 min multiple ramp [b]	230 °C
Scenario 3	60 min multiple ramp [c]	230 °C

a - 45 min multiple ramps: 40 °C hold 4 min; 10 °C/min to 270 °C hold 13 min
b - 33 min multiple ramp: 65 °C hold 1 min; 4 °C/min to 115 °C hold 1 min; 25 °C/min to 130 °C hold 0 min; 15 °C/min to 280 °C hold 1 min; and 20 °C/min to 320 °C hold 5 min
c- 60 min single ramp: at 60 °C, 4 °C/min to 300 °C
d - Adapted from USEPA 8720D Method

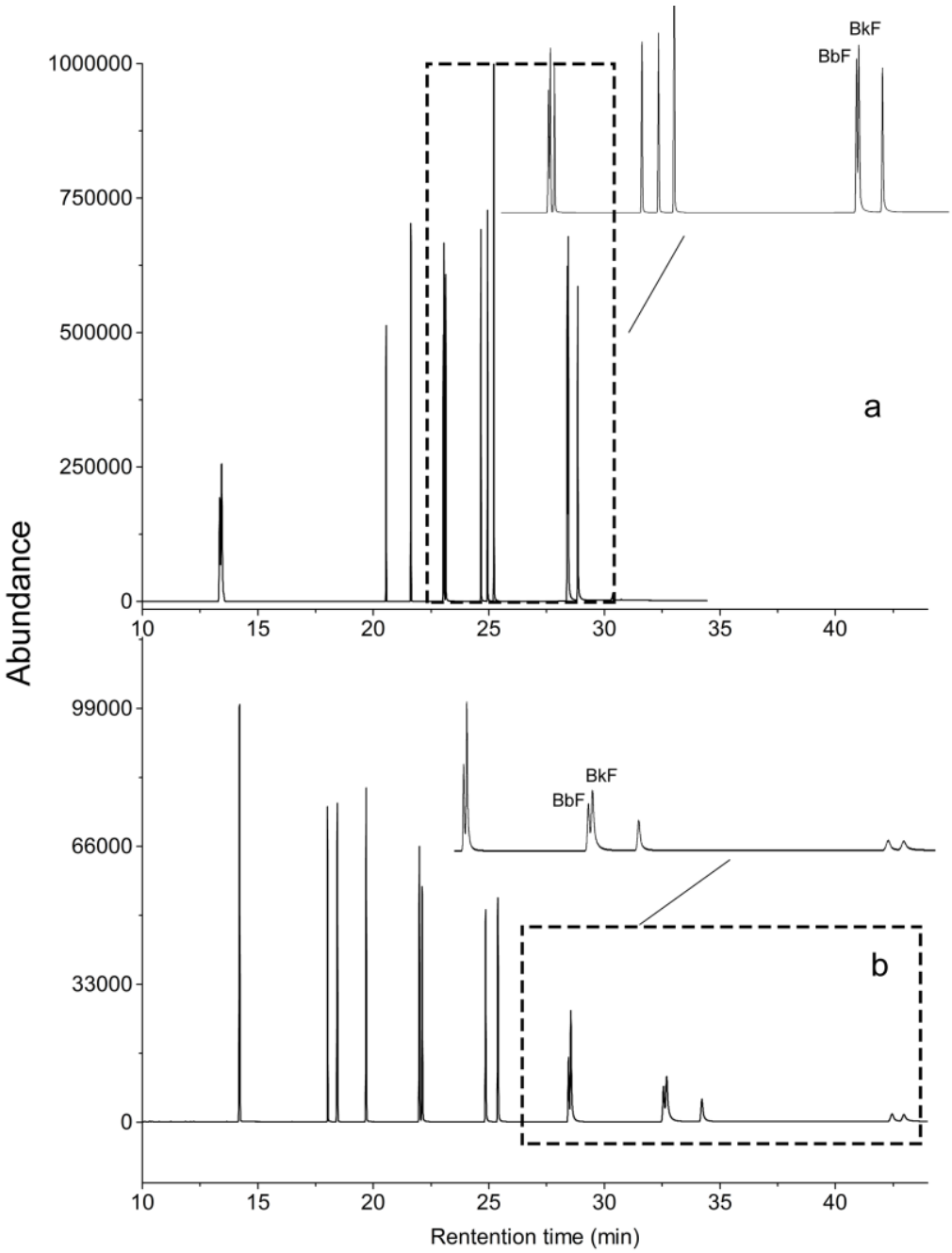


Figure 3.2 Chromatographs of PAHs for: (a) Scenario 2; (b) Scenario 1

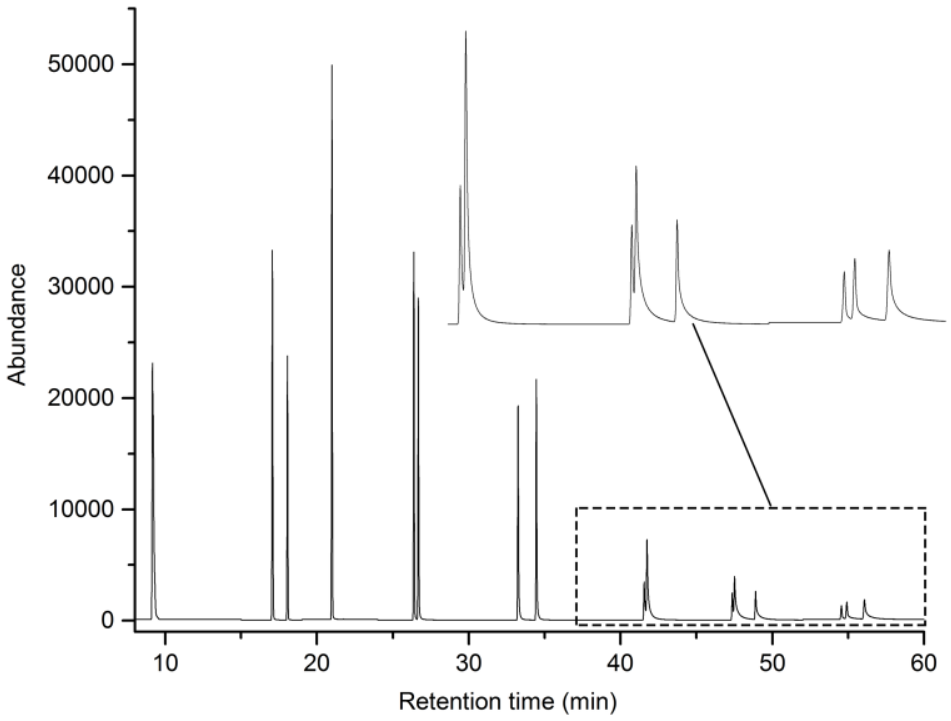


Figure 3.3 Chromatographs of PAHs for scenario 3

Ion-source adjustment

According to Prest and Thomson (Thomson *et al.*, 2007), the increase of ion-source temperature can enhance the peak abundance and reduce the peak tailing. Therefore, the performance of 350ºC ion-source was compared with 230ºC (most common setting in recent GC/MS analysis), the peaks of both settings are shown in **Figure 3.4**. Typically for the largest molecular compound of 16 PAH, the tailing had been reduced, and the peak abundance was significantly increased. The peaks of all the 16 PAHs are showing good resolution and shape even in concentration as low as 4pg (0.2ng/mL, 2μL) injection. Therefore, lower calibration range could be allowed by this setting to achieve more accurate determination in trace level detection with lower enrichment factor. The calibration range level was then reduced from 10~1000ng/mL to 0.1~20ng/mL, approximately 100 times. The comparison of external calibration in scenario 2 and normal range with the enhanced setting (scenario 3 with increased ion-source temperature) and lower range are shown in **Table 3.4**. Under the external calibration range of 0.1~20ng/mL, the enhanced setting provided the regression values range from 0.9962 to 0.9999 (0.9990 average) whereas the scenario 2 only gave us values ranged from 0.995 to 0.9995 (0.9981 average) under calibration of 10~1000ng/mL. The regression of lower calibration level was comparable or even higher than the regression of higher calibration level. This was due to the enhanced sensitivity achieved by the optimized setting. The significance of this improvement not only allow lower enrichment factor in pretreatment but also directly enhance the accuracy of quantitation in trace level detection.

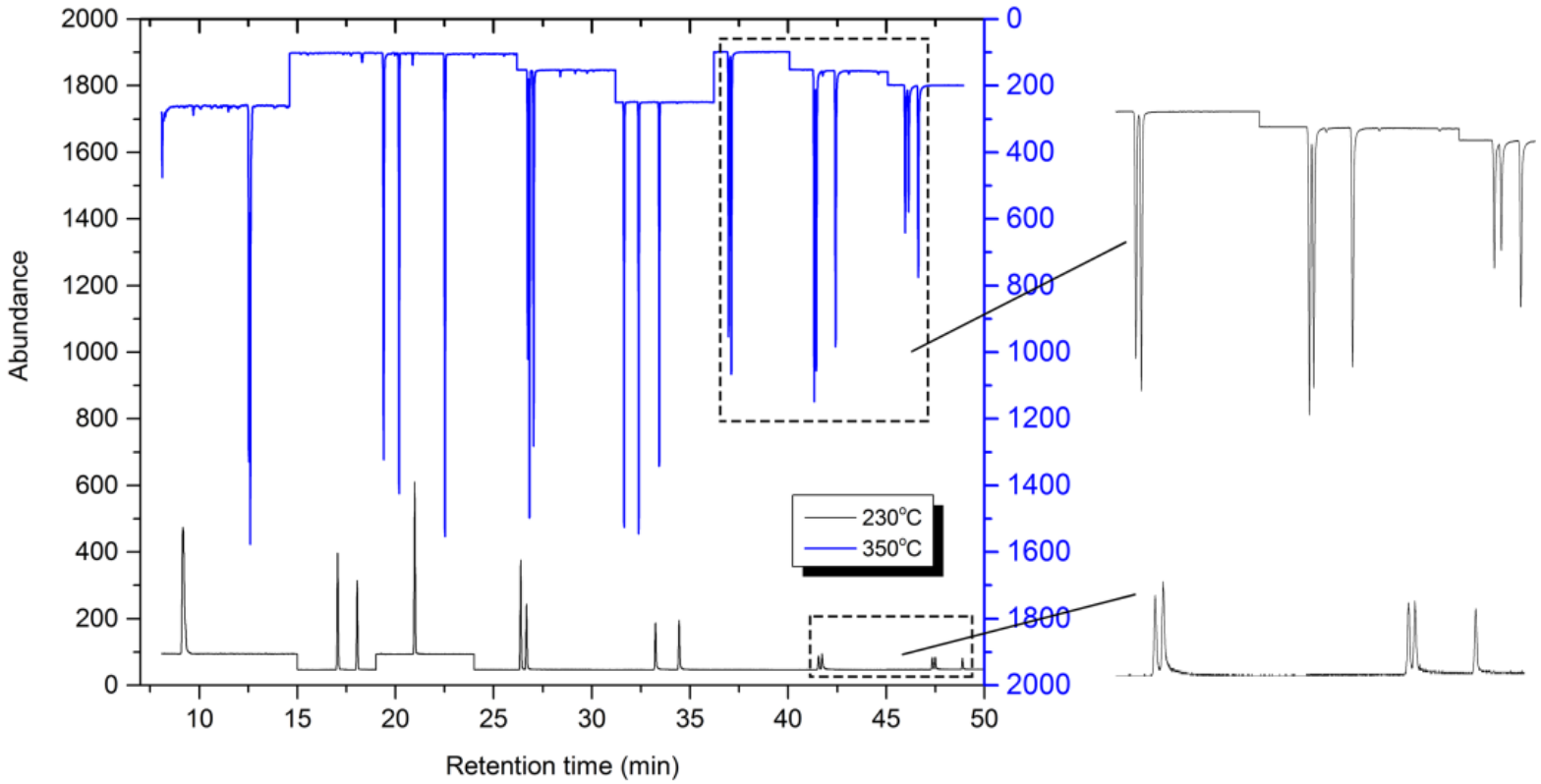


Figure 3.4 Impact of ion source temperature in scenario 3

Table 3.4 Comparison of GC/MS analyses of PAHs: retention times of studied compounds, ions monitored and method linearity ranges in the enhanced and common setting

PAHs			Scenario 2			Scenario 3 with Ion-source 350^{0}C		
	Ions (m/z) monitored for quantization	Ions (m/z) monitored for confirmation	Retention Time (33 min)	Calibration Range (ng/ml)	Linearity (R^2)	Retention time (60 min)	Calibration Range (ng/ml)	Linearity (R^2)
NAP	128	127,129	10.98	10~1,000	0.9995	11.26	0.1~20	0.9996
ACY	152	151	17.47	10~1,000	0.9995	19.55	0.1~20	0.9999
ACE	153	154	17.91	10~1,000	0.9975	20.56	0.1~20	0.9999
FLO	165	166	19.04	10~1,000	0.9995	23.53	0.1~20	0.9999
PHE	178	176	20.81	10~1,000	0.9995	28.91	0.1~20	0.9998
ANT	178	176	20.91	10~1,000	0.9990	29.2	0.1~20	0.9997
FLA	202	200	22.83	10~1,000	0.9990	35.74	0.1~20	0.9998
PYR	202	200	23.19	10~1,000	0.9985	36.92	0.1~20	0.9998
CHR	228	226	25.16	10~1,000	0.9990	44.01	0.1~20	0.9986
BaA	228	226	25.21	10~1,000	0.9975	44.19	0.1~20	0.9985
BbF	252	250,253	27.05	10~1,000	0.9980	49.79	0.1~20	0.9987
BkF	252	250,253	27.1	10~1,000	0.9950	49.93	0.1~20	0.9962
BaP	252	250,253	27.55	10~1,000	0.9965	51.3	0.1~20	0.9985
DahA	276	277,274	29.11	10~1,000	0.9985	56.35	0.1~20	0.9993
IcdP	278	274	29.16	10~1,000	0.9975	56.62	0.1~20	0.9984
BghiP	276	274,277	29.51	10~1,000	0.9965	57.35	0.1~20	0.9981

3.3.2 Determination of Extraction Solvent Volume

The volume of solvent can significantly affect the extraction performance. Lower solvent volume leads to the increase of the EF by decreasing the ratio between organic/aqueous phases (Saraji and Boroujeni, 2014). In this study, the sample volume was fixed as 10 mL and the volume of solvent varies from 250 μL to 1 mL. As shown in **Figure 3.5**, the average of EFs was decreased when the solvent volume was increased. This result indicated that the even at the lowest level (250 μL), sufficient extraction efficiency was achieved for transferring PAHs from water to the organic phase. Although an even higher average of EFs could be reached if the solvent volume is lower than 250 μL, the treatment can cause difficulties of collecting the organic phase effectively from the bottom of the water sample using a syringe. Therefore, 250 μL was selected as the volume of dichloromethane for extracting 16 PAHs from the water samples. After the sample pre-treatment using VSA-LLME, 100 ± 10 μL of the organic phase was obtained in each sample.

3.3.3 Determination of Ionic strength, Shaking Time and Centrifuge Speed

The effect of three factors including the ionic strength, shaking time and centrifuge speed on VSA-LLME was investigated in this study. A DOE method was adopted to optimize the three factors and investigate their interactions. The EY outputs of the 8 experimental runs based on the DOE (**Table 3.1**) are listed. Through using the ANOVA analysis (Lundstedt et al. 1998), the effects of three targeting operation factors on VSA-LLME performance and their interactions were shown in **Figure 3.6**.

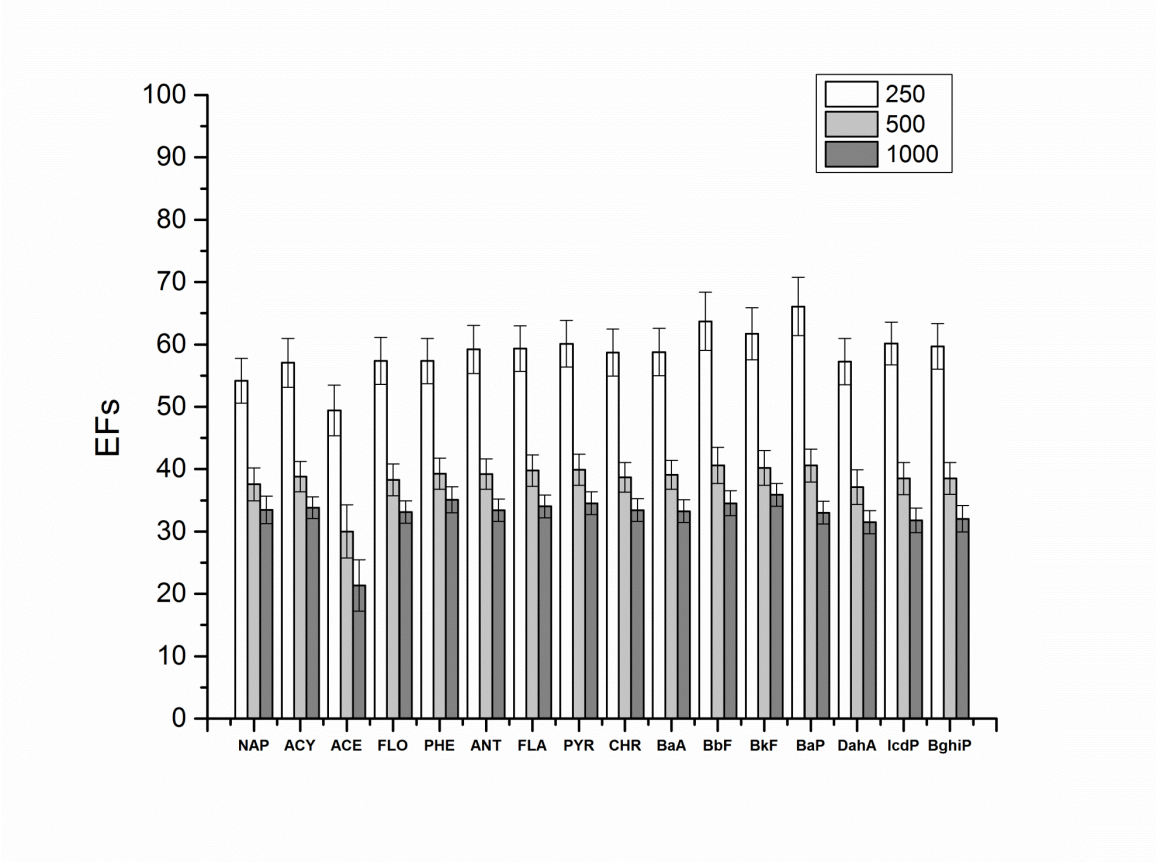


Figure 3.5 Effects of addition of extraction solvent at different levels (250, 500, 1000 µL) on VSA-LLME performance

(Conditions: addition of 0.5g NaCl, shaking for 5 minutes at 1000 rpm, and centrifuge for 5 minutes at 1000rpm)

The result shows that the p-value of the DOE model is 0.0448 (< 0.05). It indicated that the model is significant and capable of modeling the relationship between the response and factors.

Effect of Shaking Time

Shaking time was set as extraction time after emulsion formed by vortex and before the emulsion breaking by centrifuge. The shaker was used at this step to help to stabilize the fine droplets of solvent. The longer the shaking time, the more an analyte is transferred to the organic phase till the equilibrium status is achieved. The results indicated that shaking time had an insignificant positive effect on VSA-LLME performance in the range of 5 minutes to 15 minutes, but a longer extraction time did slightly enhance the extraction efficiency. Therefore, a longer shaking time (15 minutes) was adopted.

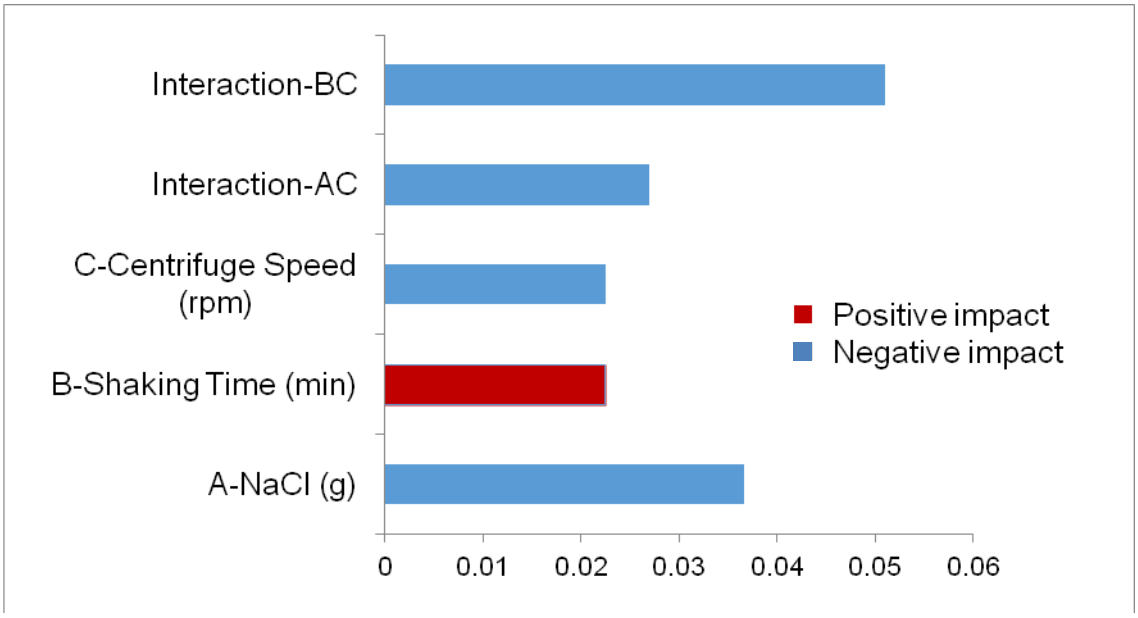


Figure 3.6 Effects of three operation factors and their interactions achieved based on two-level factorial design on VSA-LLME performance

Effect of Ionic Strength

Ionic strength is related to the "salting out effect" phenomena which can change the partition of an analyte between water and organic phases (Sarafraz-Yazdi and Amiri, 2010). Theoretically, the addition of sodium chloride could decrease the solubility of an analyte and the extraction solvent in water. The increase of ionic strength of a water sample can enhance the partition of an analyte to the organic phase so as to improve the extraction efficiency and thus increase the EY value (Zacharis *et al.*, 2012). On the contrary, the increased ionic strength may decrease the extraction efficiency during sample pre-treatment by LPME (Hou and Lee, 2004; Gioti *et al.*, 2005; Casas *et al.*, 2006). In this study, the ionic strength was adjusted using NaCl with the concentration varies from 5% to 10% (w/v) and the effect of ionic strength on VSA-LLME performance was examined. The lowest level of ionic strength was set to 5% based on the data of offshore produced water samples collected. Results showed that the addition of sodium chloride had an insignificant negative effect (**Figure 3.6**) on EY, indicating that the increased ionic strength led to the reduced extraction efficiency. This result was in agreement with several previous LPME studies. The addition of sodium chloride was thus not further applied.

Effect of Centrifuge speed

Centrifuge treatment is required for the breakdown of emulsification and phase separation. The centrifuge speed was adjusted in the range of 1000-3000 rpm, and the effect of centrifuge speed on VSA-LLME performance was investigated. Centrifuge time was set for 5 minutes. The results in **Figure 3.6** showed that the centrifuge speed had an insignificant negative effect on the EY value, and a higher centrifuge speed led to a reduced

extraction efficiency. Also, the interaction between the centrifuge speed and shaking time had a significant adverse effect on EY although the shaking time itself had shown a positive effect. It means that with a longer shaking time, the increased centrifuge speed can significantly reduce the EY. The 1000 rpm was thus selected as the appropriate centrifuge speed. Overall, the results led to the following optimized conditions for VSA-LLME treatment: non-NaCl addition; 15 minutes shaking at 1000 rpm and 5 minutes' centrifuge at 1000 rpm.

3.3.4 Analytical Performance

For validating the developed VSA-LLME method in determination of trace levels of PAHs in water samples, the method linearity, limits of detection (LOD), repeatability and recoveries were examined.

Method Linearity

Linearity is the ability to induce a signal that is directly proportional to the analyte. The linear relation between response and each PAH concentration can be investigated for the method as a whole and thus be an investigation of trueness as a function of the concentration of the analyte (Charalabaki *et al.*, 2005). The graphical shape of calibration curves (linearity/non-linearity) is examined by analyzing calibration standards that cover the entire desired measuring range. As shown in **Figure 3.7**, method calibration curves were generated by spiking water samples with five different concentration levels (10, 20, 50, 100, 200 ng/L) of the 16 PAHs. Four replicates were applied for each analysis to reduce the instrumental error. As shown in **Figure 3.7**, the result indicated that in the studied

concentration range, the VSA-LLME method showed excellent linearity for testing all the 16 PAHs in water samples. The coefficients of determination (R^2) for the obtained calibration curves were all higher than 0.99.

LODs

The calculation of LODs was conducted by using following equation:

$$\mathrm{LOD} = t_{(n-1,1-\alpha=0.99)} \times \sigma \qquad (3)$$

Where σ is the standard deviation calculated from n spiked replicate samples, and t(n-1, 1-α=0.99) is the t value at n-1 degrees of freedom with the confidence level of 1-α (99%). In this study, 7 replicated samples were analyzed for LODs determination. When n = 7, t(n-1, 1-α=0.99) = 2.143. As shown in **Table 3.5**, the LODs of the optimized VSA-LLME were in the range of 2-5 ng/L.

Repeatability

Repeatability represents the precision of a method. It is a degree of conformity between independent measurement results obtained by the same method on identical samples in the same laboratory, by the same operator, with the same equipment and within short of time. The Relative Standard Deviation (RSD%) were used as an indicator for repeatability. The following equation was for the calculation of RSD%,

$$RSD\% = \frac{\sigma_{org}}{\overline{C_{org}}} \times 100 \qquad (4)$$

Where the mean C_{org} was obtained by averaging determined PAH concentration in the organic phase of 4 replicate water samples that were initially spiked with 16 PAHs to reach a concentration of 0.2 µg/L for each PAH; and σ_{org} is the standard deviation of analyte concentration in the organic phase (C_{org}) of the 4 replicated water samples. The RSD%s of the VSA-LLME method was ranged from 6% to 11%.

EF and Recovery

Recovery can be examined through the detection of a known amount of an analytical parameter added to the water matrix and included throughout the method of analysis. After deducting any detected content of the analytical parameter in question in the original water matrix, the recovery percentage (ER%) can be calculated as a proportion of the PAH amount added. The recovery can help to evaluate the overall effect (bias) of the VSA-LLME treatment. Accuracy is estimated from the recovery of spiked PAH analytes in the matrix of interest. ER% was determined using the equation 5 To examine recoveries:

$$ER\% = \frac{\overline{C_{org}} \times V_{org}}{C_{aq} \times V_{aq}} \times 100 \qquad (5)$$

where the mean Corg was obtained by averaging determined concentrations of PAHs in the organic phase of 4 replicate water samples that were initially spiked with 16 PAHs to reach a concentration of 0.2 µg/L for each PAH; V_{org} was the volume of the organic extract. Caq and Vaq were the concentration of each PAH analyte in water solution and the volume of water solution, respectively. Results showed that the EFs of the VSA-LLME method were ranged from 68 to 78 and the recoveries were in the range between 74% and 85%.

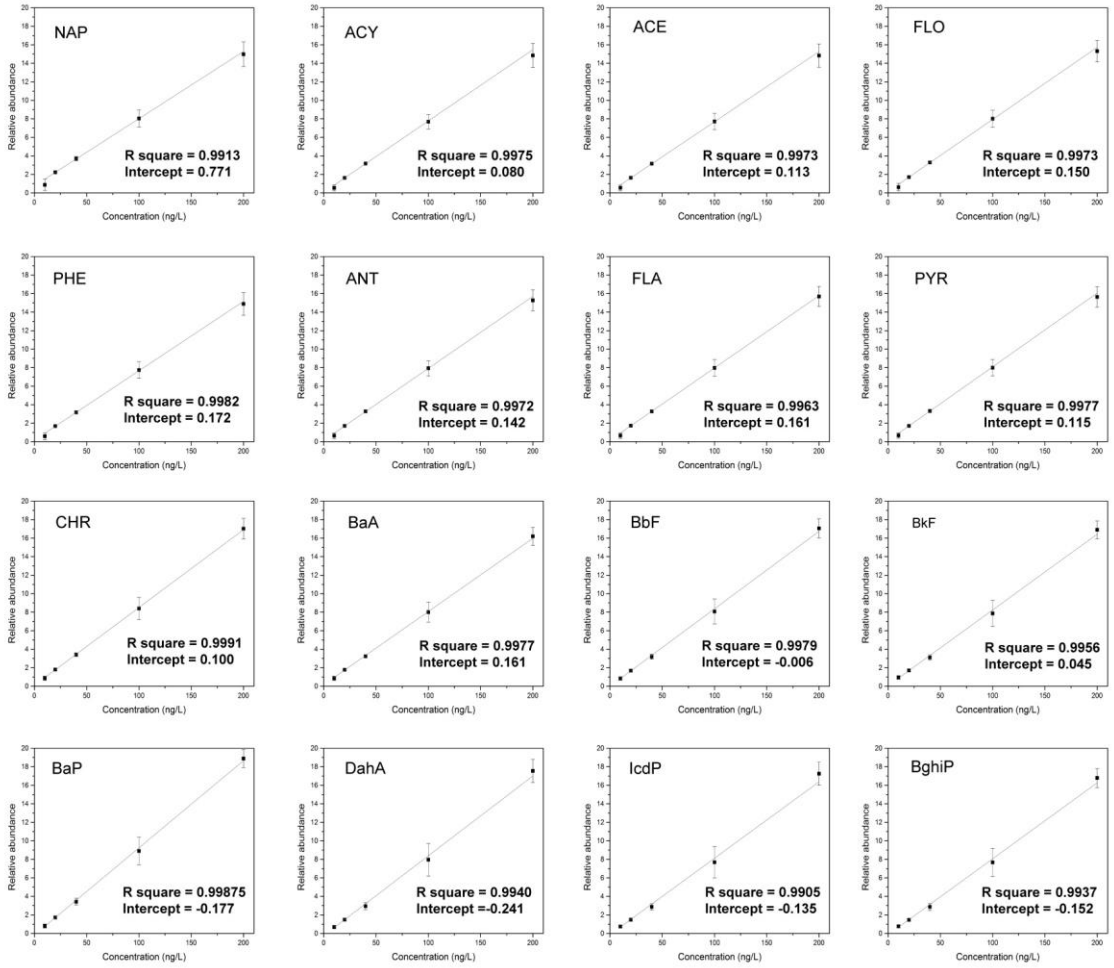


Figure 3.7 Linearity of the VSA-DLLME coupled with GC-MS method for 16PAH determination

Table 3.5 Linearity, EFs, LODs repeatability and recoveries of VSA-LLME

PAHs	Efs	LODs	Linearity Range	R^2	Recoveries[a]	Repeatability (n=4)	Recoveries in OPW[a,b]	Repeatability in OPW[b] (n=4)
		(ng/L)	(ng/L)		ER(%)	RSD (%)	ER(%)	RSD (%)
NAP	74	2	10-200	0.9913	82	6	—	—
ACY	75	2	10-200	0.9975	82	7	79	2
ACE	76	2	10-200	0.9973	83	8	79	7
FLO	78	2	10-200	0.9973	85	8	97	9
PHE	75	2	10-200	0.9982	82	8	95	11
ANT	76	2	10-200	0.9972	83	7	79	11
FLA	76	2	10-200	0.9963	83	7	81	10
PYR	76	3	10-200	0.9977	84	8	80	14
CHR	73	3	10-200	0.9991	81	8	81	8
BaA	69	3	10-200	0.9977	76	8	83	10
BbF	70	2	10-200	0.9979	77	7	81	9
BkF	68	3	10-200	0.9956	74	7	77	8
BaP	76	3	10-200	0.9988	84	6	79	10
DahA	71	5	10-200	0.9940	78	11	73	8
IcdP	71	5	10-200	0.9905	78	10	74	8
BghiP	68	5	10-200	0.9937	74	7	72	7

[a]spiked level = 0.2 μg/L
[b]offshore produced water

3.3.5 Analysis of Offshore Produced Water Samples

The offshore produced water samples have high salinity and petroleum hydrocarbon content (mostly short chain carboxylic acids) (Fakhru'l-Razi *et al.*, 2009). The developed VSA-LLME method was applied for the analysis of offshore produced water samples for the method validation in a complex matrix. After the analysis, the recovery rates within the produced water sample matrix were ranged from 72-97% (**Table 3.5**). Recoveries for most PAHs in offshore produced water samples were comparable to those in distilled water. The immiscible carboxylic acids in the produced water samples helped to stabilize the fine solvent droplets. As shown in **Figure 3.8**, after settling the clouded droplets for 5 minutes, the diameter of the droplets in produced water samples was about one-third of that in the distilled water. This result led to the increased interfacial area and decreased gradient distance for mass transfer during shaking, resulting in a more efficient extraction and a higher recovery. The function of the acids is similar as the dispersion solvent in DLLME (Saraji and Boroujeni, 2014). The results also showed that the repeatability was slightly influenced by the complex matrix of the produced water samples and the RSD%s were slightly increased to 2-14%. **Figure 3.9** illustrated a representative GC-MS chromatogram of the 16 PAHs in an offshore produced water sample. The results demonstrated the no peak interference occurred in quantification with the offshore produced water matrix.

Table 3.6 Comparison of VSA-LLME with other pre-treatment methods

Pretreatment methods	Analytical instrument	Analytes	Linear range (μg/L)	LODs (μg/L)	Extraction consumable	Average extraction time for each sample (min/sample)	Compatibility for automated injection	Ref.
SPME	GC-MS	16 PAHs	0.01-10	0.001-0.029	SPME needle	45	Yes	(King *et al.*, 2004)
HS-SDME	HPLC-FLD	5 PAHs	0.3-50; 0.05-5; 0.01-1.25; 0.7-50	1.5-28	10 μL β-cyclodextrin;	10	No	(Y. Wu *et al.*, 2008)
HF-LPME	GC-MS	5 PAHs	0.5-50	0.005-0.011	3 μL tolune, hallow fibre	15	Yes	(Charalabaki *et al.*, 2005)
SBSE	HPLC-FLD	16 PAHs	from 0.0002-0.2 to 0.002-200	0.0002-0.002	150 μL acetonitrile; stir bar	70	Yes	(Popp *et al.*, 2001)
USAEME	GC-MS	16 PAHs	—	0.001-0.036	100 μL Chloroform	15	Yes	(Ozcan *et al.*, 2010)
UDSA-DLLME	GC-MS	11 PAHs	0.08-100	0.022-0.060	14 μL heaptanol	less than 3	No	(Tseng *et al.*, 2014)
WLSEME	GC-MS	11 PAHs	0.08-100	0.022-0.13	9 μL nonanol; 240 μL 1 mg/L Triton X-100	a few seconds	No	(Tseng *et al.*, 2014)
VSA-LLME	GC-MS	16 PAHs	0.002-0.2	0.002-0.005	250 μL dichloromethane	1-15	Yes	Present study

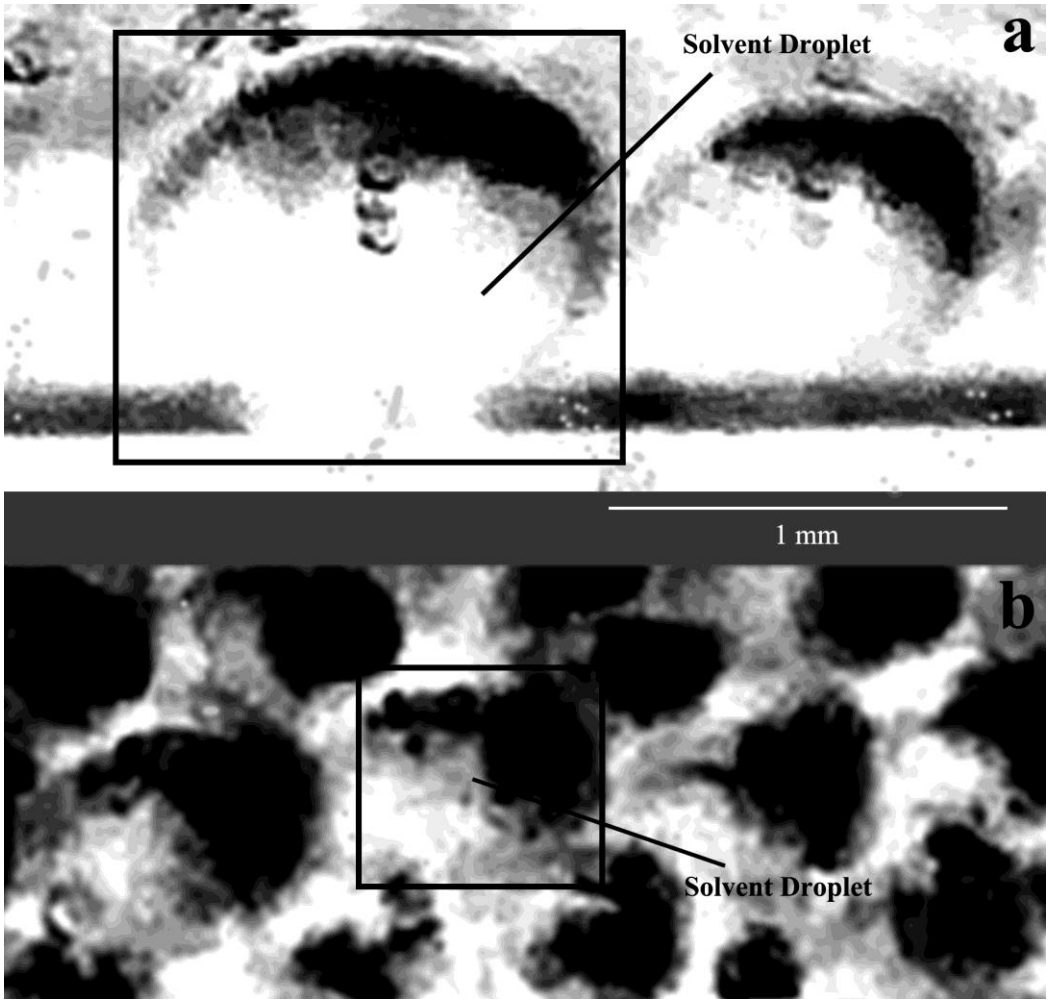


Figure 3.8 The solvent droplet sizes after vortex treatment for 10 seconds followed by a 5-min settling
a) distilled water; b) produced water

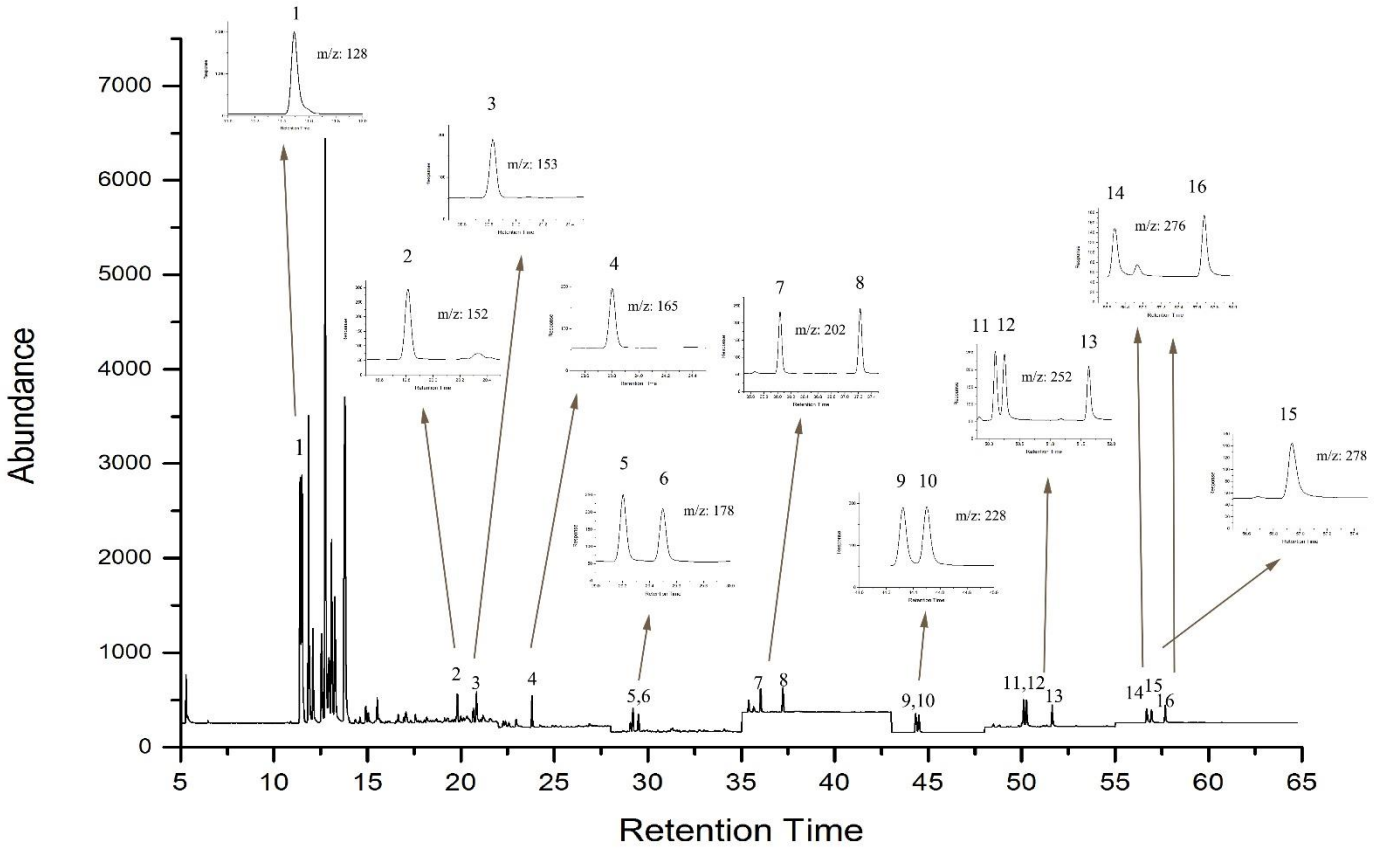


Figure 3.9 GC-MS (SIM) chromatogram of 16 PAHs spiked in offshore produced water (0.2 µg/L) after VSA-LLMD
1)NAP; 2)ACY; 3)ACE; 4)FLO; 5)PHE; 6)ANT; 7)FLA; 8)PYR; 9)CHR; 10)BaA; 11)BbF; 12)BkF; 13)BaP; 14)DahA; 15)IcdP; 16)BghiP

3.3.6 Comparison with other Analytical Methods

The performance of the VSA-DLLME method was compared with that of other advanced extraction methods. To date, there are many pretreatment methods for PAHs analysis. As shown in **Table 3.6**, the linearity range of developed method starts from 0.002 ppb, which indicates the very high sensitivity. The LOD of the developed method is lower than 0.005 ppb, which also validates its high accuracy and sensitivity. The only technique that has significantly higher sensitivity (linearity range from 0.0002 ppb and lower detection limit (below 0.002 ppb) is stir bar sportive microextraction (SBSE), which is much more expensive and time-consuming. Popular liquid phase microextraction methods include headspace single drop microextraction (HS-SDME), UD-SA-DLLME, and water with a low concentration of surfactant in dispersed solvent-assisted emulsion dispersive liquid-liquid microextraction (WLSEME). The HS-SDME offers higher LODs and requires careful sample handling which can lead to difficulties for routine analysis. USAEME shows comparable sensitivity but consumes more energy, and the ultrasound energy could degrade the analytes. UD-SA-DLLME requires the addition of additional polar solvent and its sensitivity be lower than the developed VSA-DLLME method. WLSEME applies surfactant as a dispersive solvent which might be problematic for GC.

3.4 Summary

In this study, a sample pre-treatment method namely VSA-LLME has been developed to aid the determination of trace levels of 16 PAHs in offshore produced water samples.

The parameters including solvent volume, shaking time, ionic strength and centrifuge speed were optimized. The method validation was achieved by examination of the linearity, LODs, and repeatability. Results indicated that the developed method allows determination of trace levels of dissolved PAHs with high recoveries and repeatability, as well as excellent accuracy and precision in offshore produced water matrix. The VSA-LLME method, when coupled with GC-MS, has shown a great potential for monitoring water samples containing PAHs in the marine environment.

CHAPTER 4 UV PHOTOLYSIS OF PAHS IN OFFSHORE PRODUCED WATER

4.1 Background

Polycyclic aromatic hydrocarbons (PAHs) are environmentally persistent and toxic, which can enter marine environments with offshore produced water (Manoli and Samara, 1999). They are considered the largest contributor of offshore produced water's toxicity (Neff *et al.*, 2006). As a promising technology for offshore produced water treatment, advanced oxidation processes (AOPs) have been widely applied in treating municipal and industrial wastewater in recent years, and can lead to direct and indirect photo-oxidation of the organic compounds (Javier Benitez *et al.*, 2004). Compared with traditional wastewater treatment technologies such as chlorination and biological treatment, AOPs are more efficient in treating low concentration and trace level persistent organic pollutants with less production of toxic by-products (Köhler *et al.*, 2006). Direct photolysis as a common component of AOP is also efficient in decomposing a broad range of persistent organic compounds in industrial wastewater (Beltrán *et al.*, 1996; Stasinakis, 2008). Many research apply first-order kinetics to find a approximated solution for kinetic analysis (Beltrán *et al.*, 1997; Shemer and Linden, 2007; Manoli and Samara, 2008; Mondal and Wickramasinghe, 2008; Cottrell *et al.*, 2013; Santiago-Morales *et al.*, 2013; Jing *et al.*, 2014b) in which constant light attenuation coefficients are assumed. Virtually, the light attenuation coefficients of offshore produced waters can be significantly changed during the photolysis process; thus, the dynamics of light screening can cause significant errors in modeling the degradation process. However, there is rare study or model tackled this challenge.

To fill this gap, a kinetic model, and a derived semi-empirical model were developed in this study for the first time, which can be further used to analyze and simulate the direct

photolysis process of PAHs in offshore produced water. The developed kinetics was validated by the experiments employing potassium iodide (KI) solution spiked with a relative high concentration of naphthalene (NAP) as the target water sample. Then kinetic analysis for PAHs' degradation in offshore produced water was conducted by applying this validated kinetic model. Also, a semi-empirical model was developed for achieving better simulative performance by involving the transformation of the previously developed model and finite element method (FEM) concept.

4.2 Methodology

4.2.1 Kinetic Development

According Stark-Einstein law, the direct photolysis process can be described by the following equation:

$$r = -\frac{dC}{dt} = \phi I_a \qquad (1)$$

Where r is the rate of reaction ($M \cdot s^{-1}$), C is the concertation of reactant ($M \cdot L^{-1}$), t is the treatment time (s), I_a is the irradiance intensity of light absorbed by the reactant ($eistain \cdot L^{-1} \cdot s^{-1}$), and ϕ is a unitless factor that refers to the quantum yield of the reactant. By combining equation 1 with the Lambert-Beer law (Beltran, Ovejero, and Acedo 1993) to substitute the absorbed irradiance to the function of concentration (2.303 was assumed to be equal to ln10), the following classic equation can be obtained for solely absorbing species with unique light wavelengths:

$$-\frac{dC}{dt} = \phi I_0[1 - \exp(-2.303C\epsilon b)] \qquad (2)$$

Where I_0 is the initial intensity of light irradiance (einstein·L^{-1}·s^{-1}), b is the light path length (cm), and ϵ is the extinction coefficient via the light wavelength of the reactant (M^{-1}·cm^{-1}). When multiple light absorbing species present in water, the rate of reaction for the target reactant (i.e. a PAH) can be expressed by introducing light screening effect:

$$-\frac{dC_{PAH}}{dt} = \phi I_0 f_{PAH}[1 - \exp(-2.303b(\sum_{i=1}^{n} C_i\epsilon_i + C_{PAH}\epsilon_{PAH}))] \qquad (3)$$

Where C_i and ϵ_i are the concentrations and extinction coefficients of different light absorbing species in water except for the target. f_{PAH} is the fraction of light absorbed by the target reactant which can be calculated by the following equation:

$$f_{PAH} = \frac{C_{PAH}\epsilon_{PAH}}{\sum_{i=1}^{n} C_i\epsilon_i + C_{PAH}\epsilon_{PAH}} \qquad (4)$$

To introduce the light screening dynamics of substrate into the model, assumptions were made to simplify the system. The sample matrix (also refers to substrate which means the components in the sample other than the target) is assumed to behave as a unique light-absorbing species with concentration C_M, extinction coefficient $\epsilon_M = \epsilon_{PAH}$ and hypothetic quantum yield ϕ_M. So the attenuation coefficient of the matrix (μ_{sample}) is equal to the product of C_M and $\epsilon_{PAH,}$ and the equation 4 can be converted to:

$$f_{PAH} = \frac{C_{PAH}\epsilon_{PAH}}{C_M\epsilon_{PAH} + C_{PAH}\epsilon_{PAH}} = \frac{C_{PAH}}{C_M + C_{PAH}} \qquad (5)$$

By applying differentiation for equation 5 via irradiation time t, following the relationship between f_{PAH} and t can be obtained:

$$\frac{df_{PAH}}{dt} = \frac{\frac{dC_{PAH}}{dt}C_M - \frac{dC_M}{dt}C_{PAH}}{(C_M + C_{PAH})^2} \qquad (6)$$

In the case of degradation of trace pollutants in wastewater with high light attenuation, following conditions can be assumed: the target just absorbs a very small fraction of light

irradiance, which can be expressed as $f_{PAH} << 1$, $f_M \approx 1$; the total absorbance of wastewater is high, which can be expressed as $(C_M \cdot \epsilon_{PAH} + C_{PAH} \cdot \epsilon_{PAH}) \cdot b > 2$, $I_a \approx I_0$ (Beltran, Ovejero, and Acedo 1993). Then, the equation 3 can be rewritten to:

$$-\frac{dC_{PAH}}{dt} = \phi_{PAH} f_{PAH} I_0 \qquad (7)$$

$$-\frac{dC_M}{dt} = \phi_M I_0 \qquad (8)$$

By combining the equation 6, 7 and 8, following equation can be derived:

$$\frac{df_{PAH}}{dt} = \frac{\phi_M I_0 C_{PAH} - \phi_{PAH} f_{PAH} I_0 C_M}{(C_M + C_{PAH})^2} \qquad (9)$$

By transformation of the equation 5, the C_M can be expressed as:

$$C_M = \left(\frac{1}{f_{PAH}} - 1\right) C_{PAH} \qquad (10)$$

By substitution, the equation 9 can be further converted to:

$$\frac{df_{PAH}}{dt} = \frac{I_0 {f_{PAH}}^2 [\phi_M - \phi_{PAH}(1 - f_{PAH})]}{C_{PAH}} \qquad (11)$$

Based on the assumption of $f_A << 1$, equation 11 can be further simplified to:

$$\frac{df_{PAH}}{dt} = \frac{I_0 {f_{PAH}}^2 (\phi_M - \phi_{PAH})}{C_{PAH}} \qquad (12)$$

By combining the equation 7 and 12, the following relationship between C_{PAH} and f_{PAH} can be obtained:

$$\frac{df_{PAH}}{f_{PAH}} = \left(1 - \frac{\phi_M}{\phi_{PAH}}\right) \frac{dC_{PAH}}{C_{PAH}} \qquad (13)$$

By applying integration on the equation 13, the f_{PAH}'s function of C_{PAH} can be derived as follow:

$$f_{PAH(C_{PAH})} = f_{PAH,0} \cdot {C_{PAH}}^{\left(\frac{\phi_M}{\phi_{PAH}} - 1\right)} \cdot {C_{PAH,0}}^{\left(1 - \frac{\phi_M}{\phi_{PAH}}\right)} \qquad (14)$$

Where the "0" in subscript indicates the initial value. Then the equation 7 can be transformed to the following equation:

$$C_{PAH}^{(\frac{\phi_M}{\phi_{PAH}}-1)} dC_{PAH} = -\phi_{PAH} I_0 f_{PAH,0} \cdot C_{PAH,0}^{\left(\frac{\phi_M}{\phi_{PAH}}-1\right)} \cdot dt \qquad (15)$$

After integration, the C_{PAH} can be expressed by the following function of time t:

$$C_{PAH(t)} = C_{PAH,0}(1 - \frac{f_{PAH,0}\phi_M}{C_{PAH,0}} I_0 t)^{\frac{\phi_{PAH}}{\phi_M}} \qquad (16)$$

Since the absorbance of the target is much less than the total absorbance of the wastewater, $\epsilon_{PAH} C_{PAH} << \epsilon_{PAH} C_M$, the light attenuation coefficient $\mu_{sample}=\epsilon_{PAH} C_M$. Therefore, from equation 5 we can get:

$$f_{PAH,0} = \frac{C_{PAH,0}\epsilon_{PAH}}{\mu_{sample,0}} \qquad (17)$$

Thus, by substituting equation 17 to 16, following function of t for C_{PAH} can be derived:

$$\frac{C_{PAH(t)}}{C_{PAH,0}} = (1 - \frac{\epsilon_{PAH}\phi_M I_0}{\mu_{sample,0}} t)^{\frac{\phi_{PAH}}{\phi_M}} \qquad (18)$$

The equation 14 describes the light screening dynamics; the equation 15 indicates the photolysis kinetics, and equation 18 can be used to predict the concentration of target pollutant. thus, the following function of C_{PAH} regarding t can be derived:

$$C_{PAH(t)} = C_{PAH,0}(1 - \frac{\epsilon_{PAH}\phi_M I_0}{\mu_{sample,0}} t)^{\frac{\phi_{PAH}}{\phi_M}} \qquad (19)$$

Where μ_{sample} is the attenuation coefficient of wastewater and "0" in the subscript indicates that it is the initial value. ϕ_M can be defined by zero order regression and is a ϵ_{PAH} dependent factor:

$$\phi_M = \frac{-\Delta\mu_{sample}}{\epsilon_{PAH} I_0 t} \qquad (20)$$

4.2.2 Experimental Validation and Kinetic Analysis

Materials

The PAH standards were supplied by Agilent Technologies Inc, USA (p/n 8500-6035). The naphthalene (NAP) stock solution had a nominal concentration of 1000 µg/ml naphthalene. The PAH stock solution had a nominal concentration of 500 µg/ml NAP; acenaphthylene (ACY); acenaphthene (ACE); fluorine (FLO); phenanthrene (PHE); anthracene (ANT). Naphthanlene-d_8 (99%, Cambridge Isotopes Labs, Canada) and Phenanthrene-d_{10} (99%, C/D/N Isotopes Inc., Canada) were used as internal standards. The KI and solvents, including ultra-high purity water, were of reagent grade or equivalent quality and were purchased from VWR International (Mississauga, Ontario, Canada) and Fisher Scientific (Ottawa, Ontario, Canada).

Analysis

The attenuation coefficient was measured at 254 nm wavelength with a ThermoScientific® Genesys 10S UV-Vis spectrophotometer. The concentrations of PAHs were determined by the vortex and shaker assisted liquid-liquid microextraction (VSA-LLME) pre-treatment method coupled with gas chromatography and mass spectrometry (GC-MS) analysis. After sample pre-treatment, instrument analysis was performed on an Agilent® 7890A/5975C GC-MS system equipped with an Agilent 7693 auto-sampler. The detailed analytical method can be found in Zheng's previous study (Zheng et al. 2015).

UV Photolysis

The photolysis experiments were conducted using a 1 L glass jar with a quartz cover

at room temperature (i.e., 20 ºC). A 8 w low-pressure UV lamp was placed above the cover and the water chamber was air tight. The samples were collected from a port at the bottom of the jar. **Table 4.1** shows the operation parameters of the experiments.

For the validation of the developed kinetic model, 0.1 mg/L NAP and 40 mg/L KI were added into deionized water to prepare the water sample. For investigating photolysis of PAHs in deionized water, the samples were prepared by spiking 10 ppb of NAP and 0.2 ppb of ACY, ACE, FLO, PHE, and ANT. The offshore produced water sample had 6 ppb naphthalene and 220 mg/L dissolved organic carbon (DOC). Its pH and salinity were 4.8 and 42 ppt (parts per thousands), respectively. Since no other PAHs were identified in the offshore produced water sample, the other five 6 PAHs were also spiked into offshore produced water at 0.02 ppb to investigate their degradation. The initial sample volume was set as 1 L for all the UV irradiation experiments.

Table 4.1 Operation parameters of UV treatment experiment

UV Wavelength	Irradiance Area	Light Path Length	Irradiance Intensity
λ (nm)	A (cm^2)	b (cm)	I_0 (Einstein$\cdot L^{-1}\cdot s^{-1}$)
254	50	13	1.27×10^{-7}

4.3 Results and Discussion

4.3.1 Sensitivity Analysis

Among the parameters of the developed kinetic model (equation 23), only I_0 is a controllable operation parameter. The other parameters such as $\mu_{sample,0}$ and ϕ_M are related to the properties of the wastewater sample. ϕ_{PAH} and ϵ_{PAH} refer to the quantum yield and distinction coefficient of the target pollutant in wastewater, respectively. Similar to the pseudo-first-order kinetic, the removal rates were found to be not related to the initial concentration $C_{A,0}$ in this model, showing agreement with Shemer's study (Shemer and Linden, 2007). The following values were used as the base values for sensitivity analysis: $I_0 = 1 \times 10^{-7}$ einstain$\cdot L^{-1} \cdot s^{-1}$, $\Sigma_{sample,0} = 0.25$ cm^{-1}, $\phi_M = 1 \times 10^{-7}$, $\phi_{PAH} = 5 \times 10^{-3}$ and $\epsilon_{A=} 5 \times 10^3$ $M^{-1} \cdot cm^{-1}$.

According to the results (**Figure 4.1 – 4.5**), the effects of most parameters were similar to their effects in the first order kinetic, except for the hypothetic matrix quantum yields (ϕ_M). ϕ_M is closely related to the light screening dynamic which is not considered in the first order kinetic. The results in **Figure 4.5** show that higher ϕ_M can lead to higher removal rates of PAHs, especially in the period before the end. The shape of the degradation curves was also significantly changed, indicating the important role of ϕ_M for predicting the removal rates. According the results, it was found that when the value of ϕ_M was between $\pm 1 \times 10^{-7}$, $M^{-1} \cdot cm^{-1}$ the degradation trend was similar as the first order kinetic. Virtually, the first order kinetic is a special case of the proposed model for the low light screening dynamic case:

Let $\phi_A/\phi_M = a$, equation 18 in section 4.2.1 can be rewritten as:

$$\frac{C_{PAH(t)}}{C_{PAH,0}} = \left(1 - \frac{\epsilon_{PAH}\phi_{PAH}I_0}{a\mu_{sample,0}}t\right)^a = \exp\left[a \cdot \ln\left(1 - \frac{\epsilon_{PAH}\phi_{PAH}I_0}{a\mu_{sample,0}}t\right)\right] \quad (1)$$

When a $\rightarrow \infty$, since $\frac{\epsilon_{PAH}\phi_{PAH}I_0}{a\mu_{sample,0}}t \rightarrow 0$ and $\lim_{x\to 0} 1 - e^{-x} = x$

$$\lim_{a\longrightarrow\infty} \frac{C_{PAH(t)}}{C_{PAH,0}} = \lim_{a\longrightarrow\infty} \exp\left[a \cdot ln\left(1 - \frac{\epsilon_{PAH}\phi_{PAH}I_0}{a\mu_{sample,0}}t\right)\right] = \exp\left[-a \cdot \left(\frac{\epsilon_{PAH}\phi_{PAH}I_0}{a\mu_{sample,0}}t\right)\right] =$$

$$\exp(-\frac{\epsilon_{PAH}\phi_{PAH}I_0}{\mu_{sample,0}}t) \quad (2)$$

From equation 2, it can be seen that when $\phi_A >> \phi_M$ ($a \rightarrow \infty$), ϕ_M has no noticeable effect, and the removal rate can be approximated as a function of the first order kinetic as $k = \frac{\epsilon_{PAH}\phi_{PAH}I_0}{\mu_{sample,0}}$, which appear to be the same as Morales' model (Santiago-Morales *et al.*, 2013).

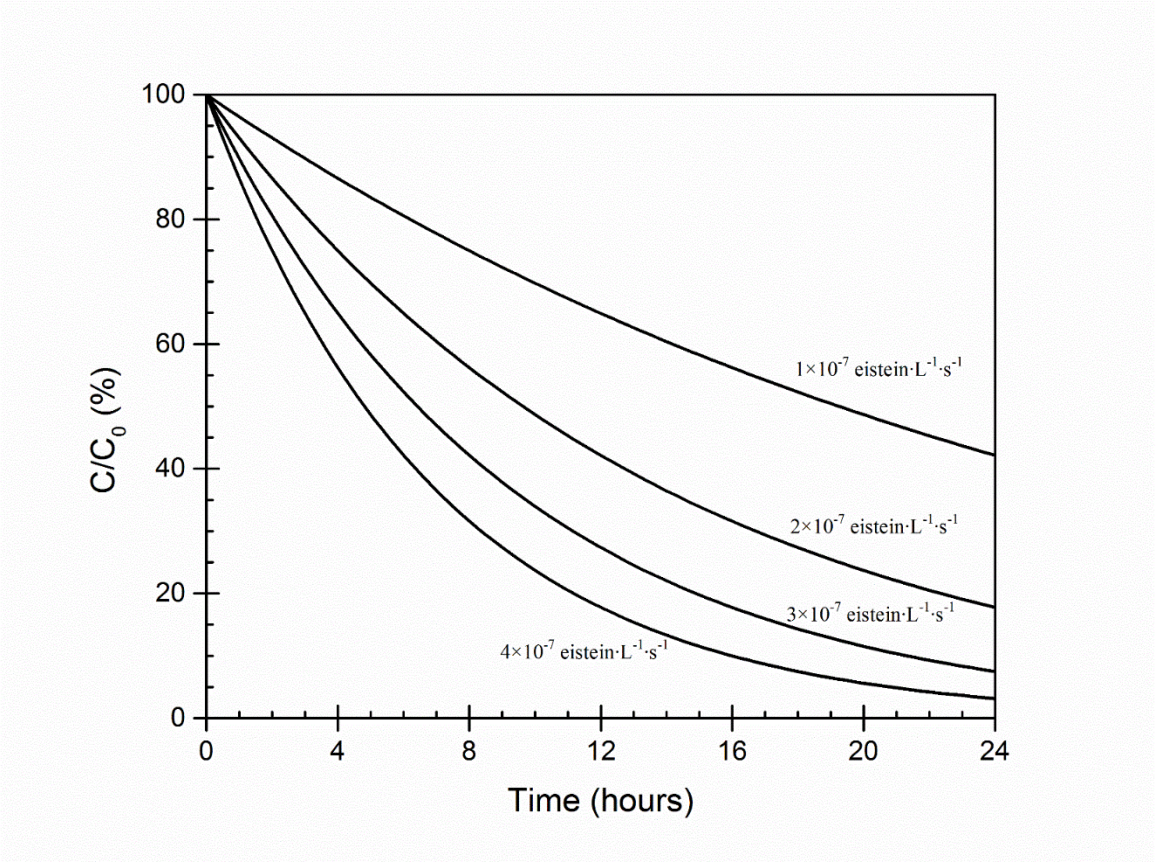


Figure 4.1 Predicted effect of irradiance intensity.

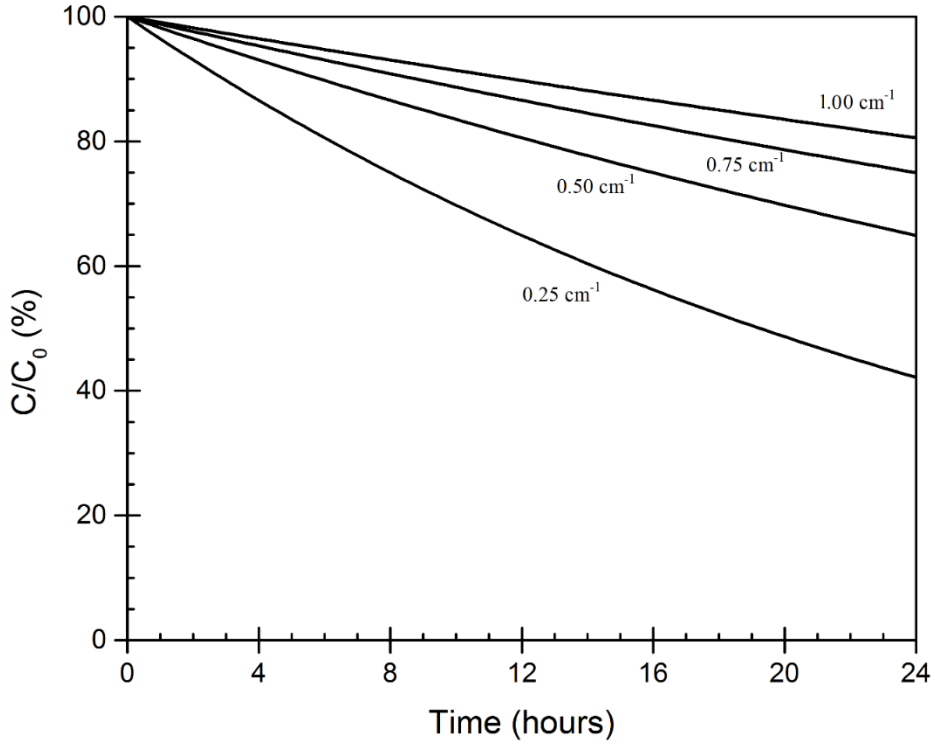


Figure 4.2 Predicted effect of matrix attenuation.

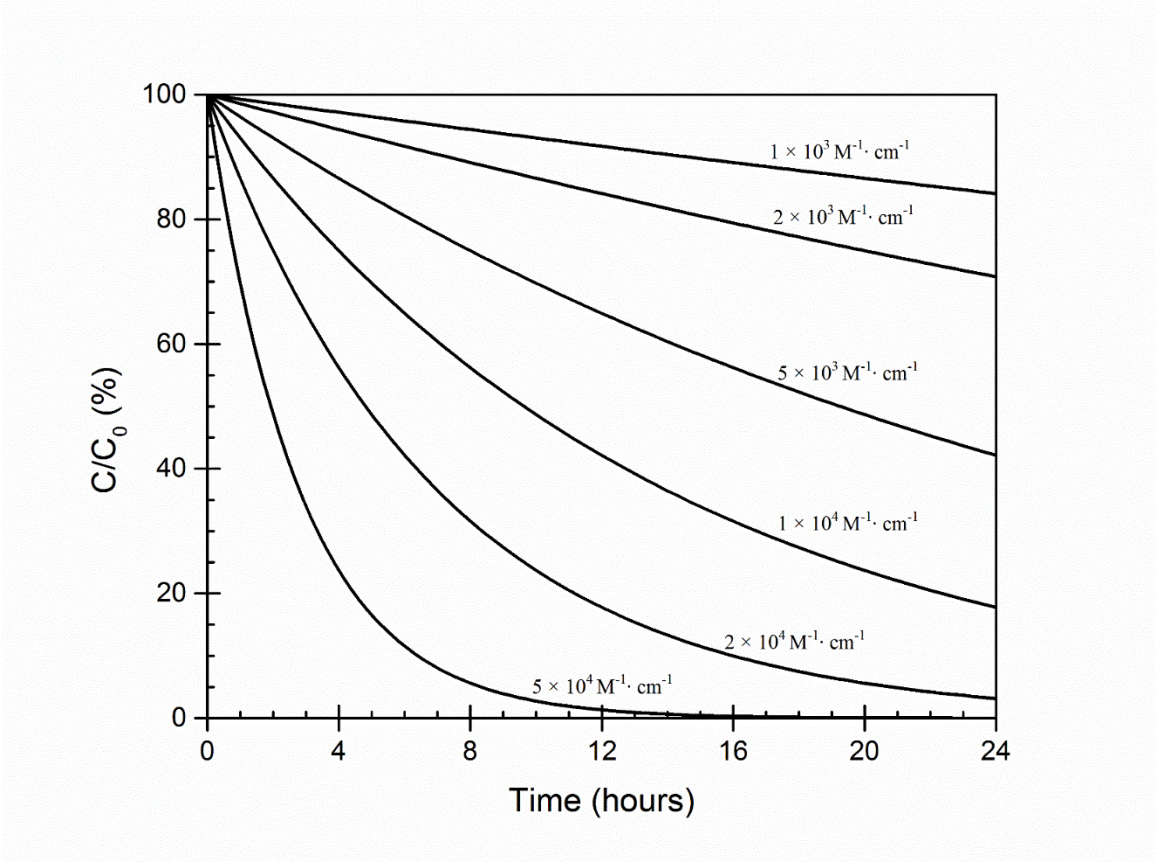


Figure 4.3 Predicted effect of distinction coefficient of target pollutant.

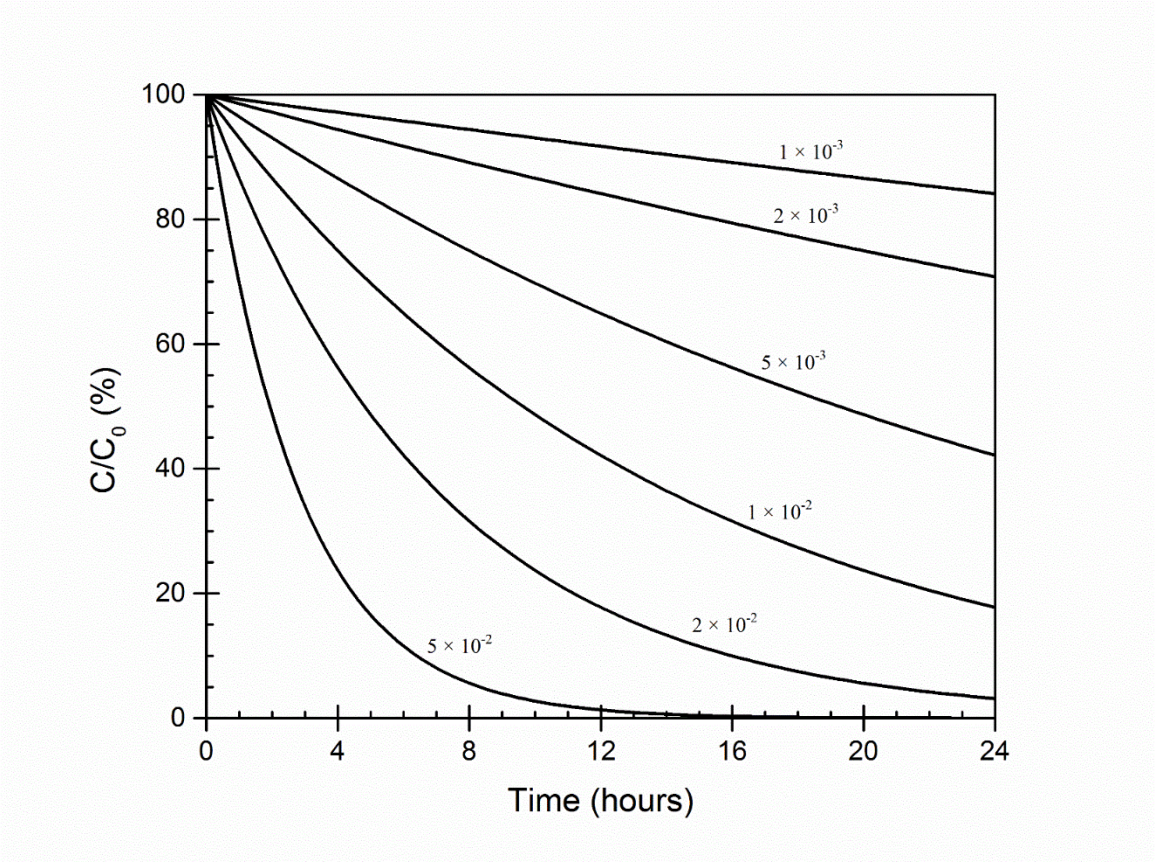


Figure 4.4 Predicted effect of quantum yield of target pollutant.

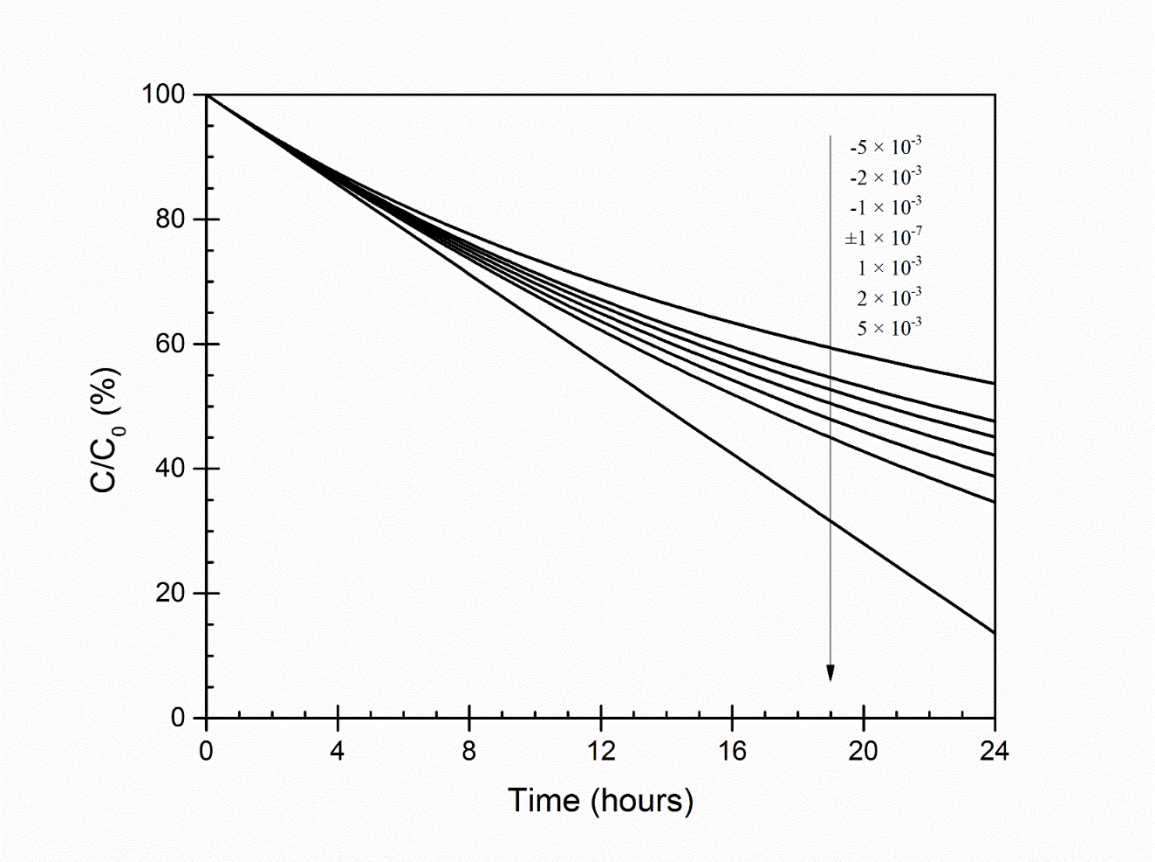


Figure 4.5 Effects of hypothetic matrix quantum yields in developed kinetic model.

4.3.2 Kinetic Model Verification

The developed model was validated by examining the degradation of NAP in KI solution. KI was selected as the competitor because of its high light absorption ability at 254 nm and its vulnerability to the UV-induced transformation (Kalmar *et al.*, 2014). Since the developed model assumes that the sample matrix of offshore produced water behaves as one species, using KI as a competitor would be appropriate to satisfy the model's assumptions. The significant change of light screening effect caused by KI solution is shown in **Figure 4.6,** and the perfect fitting of zero-order was found. According the results illustrated in **Figure 4.6**, the value of $\phi_M \epsilon_{PAH}$ was calculated to be - 8.16×10^{-3} $cm^{-1}s^{-1}$. **Figure 4.7** compares the regressions of the first order kinetic model and the developed kinetic model using experimental data. The results showed that both models offered excellent regressions. The improvement was observed for the developed model, and a high correlation coefficient (R=0.9998) between the developed kinetic model's simulation and experimental data was found. The fixed quantum yield of NAP in the developed kinetic model as 0.0954, which was slightly lower than the reference data (0.16 ± 0.02) (Schwarz and Wasik, 1976). This result may be attributed to the quenching effect of iodide ion (Fasnacht and Blough, 2003). The relative small simulative difference between the developed kinetic model and the first order kinetic model was caused by the much lower value of ϕ_M than that of NAP's quantum yield (ϕ_{PAH}). This finding further suggested that ϕ_{PAH} dominated the dynamic changing of the fraction of light irradiance absorbed by NAP (f_{PAH}).

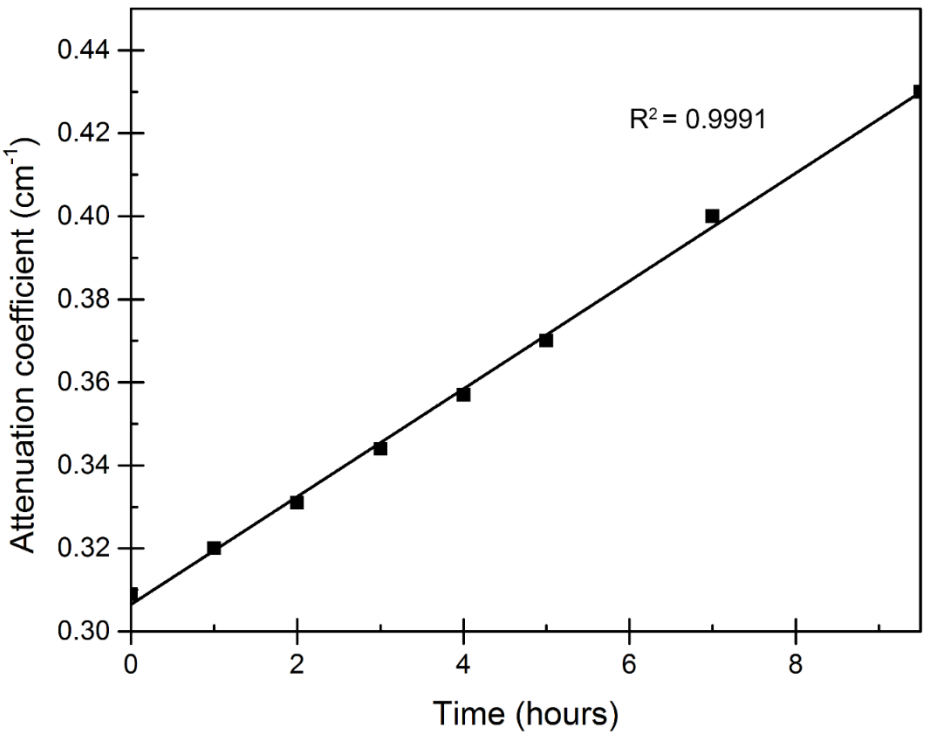


Figure 4.6 Light screening dynamics of KI solution

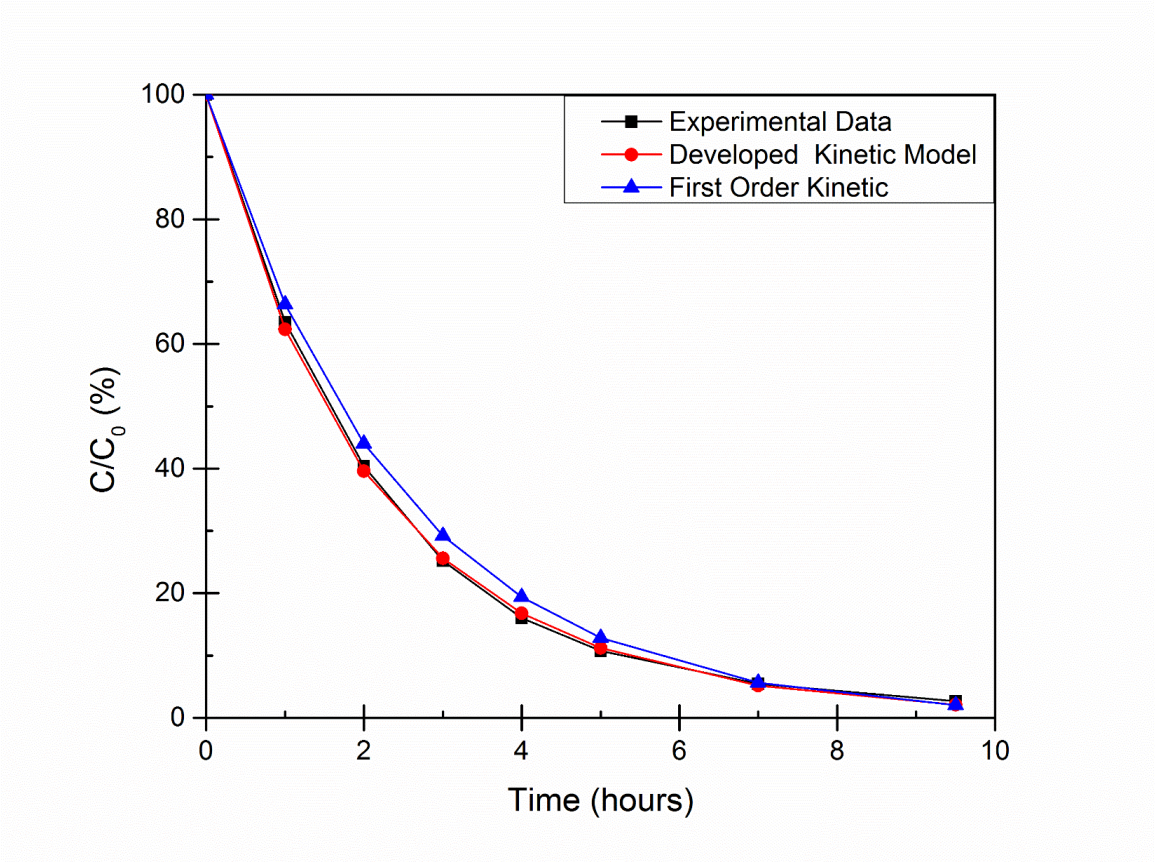


Figure 4.7 Comparison of removal rate data obtained from developed model simulation, first order kinetics and experimental observation

4.3.3 Photolysis of PAHs in Deionized Water

To compare with the photolysis in offshore produced water, the degradation rates and quantum yields of 6 small molecular weight PAHs were determined in deionized water. Acetone was used as the solvent of PAHs stock and the concentration in the sample was 1.3×10^{-4} M. The attenuation coefficient of the sample was measured to be 0.0012 cm^{-1}. Despite the increased attenuation, the light screening of acetone was not significant since the total absorbance of water sample was maintained at a relatively low level. Thus, the competition between individual PAH and acetone was not significant. This can be demonstrated by the following illustration:

$$-\frac{dC_{PAH}}{dt} = \phi I_0 \frac{C_{PAH}\epsilon_{PAH}}{\sum_{i=1}^{n} C_i\epsilon_i + C_{PAH}\epsilon_{PAH}}[1 - \exp(-2.303b(\sum_{i=1}^{n} C_i\epsilon_i + C_{PAH}\epsilon_{PAH}))]$$

Since $-2.303b(\sum_{i=1}^{n} C_i\epsilon_i + C_{PAH}\epsilon_{PAH}) = 0.036 \ll 1$,

$$-\frac{dC_{PAH}}{dt} \approx \phi I_0 \frac{2.303b(\sum_{i=1}^{n} C_i\epsilon_i + C_{PAH}\epsilon_{PAH})C_{PAH}\epsilon_{PAH}}{\sum_{i=1}^{n} C_i\epsilon_i + C_{PAH}\epsilon_{PAH}} = 2.303\phi I_0 \epsilon_{PAH} C_{PAH} b$$

The photolysis processes of 6 PAHs were fitted by using the first order kinetic. The rate constants and quantum yields are summarized in **Table 4.2**. The obtained quantum yields were majorly lower than those of other studies (Beltran *et al.*, 1995; Miller and Olejnik, 2001), which may be caused by the interactions between PAH species (Miller and Olejnik, 2001; Shemer and Linden, 2007).

Table 4.2 Photolysis of 6 PAHs in deionized water

	Constant of First Order	Quantum Yield in Deionized Water	Linear Regression of Ln(C)
	$k\ (s^{-1})$	ϕ_D	R^2
NAP	1.73×10^{-5}	1.34×10^{-3}	0.9954
ACY	6.72×10^{-5}	2.81×10^{-3}	0.9844
ACE	1.62×10^{-5}	7.75×10^{-4}	0.9960
FLO	5.98×10^{-5}	2.33×10^{-3}	0.9958
PHE	6.56×10^{-5}	1.40×10^{-3}	0.9919
ANT	1.26×10^{-4}	4.24×10^{-4}	0.9871

4.3.4 Photolysis of PAHs Offshore Produced Water

Offshore produced water has high concentrations of inorganic ions (CO_3^{2-}, NO_3^-, Fe^{2+}, I^-) and dissolved organic carbons (DOC) which can produce different reactive species during their photolysis. However, in this case, direct photolysis was the major pathway since the indirect photo-oxidation initiated by reactive species ($^1O_2$, HO·, ^{3}DOM*) played an unimportant role due to the high concentrations of scavengers (i.e. HCO_3^-, I^-, DOM, phenols) in the matrix (Scurlock *et al.*, 1990; Canonica and Freiburghaus, 2001; Fasnacht and Blough, 2003; Sirivedhin and Dallbauman, 2004; Shemer and Linden, 2007; Jacobs *et al.*, 2008). ϕ_M was determined by the initial and final values of the attenuation coefficient and ϵ_{PAH} (**Table 4.3**). The results in **Figure 4.8** indicate that the attenuation coefficient rapidly increased in the first 8 hours. This increasing trend can be explained by the following three factors: the photo-oxidation of inorganic species such as I^-, Fe^{2+} (similar as in model validation case with KI solution); the phototransformation of larger molecules into smaller products that have higher absorptivity at 254 nm; and the destruction of particulate organic matters and dispersed oil droplets that can release aqueous organic pollutants. **Figure 4.8** also show that the slope of attenuation coefficient was decreased to 3.6×10^{-7} $cm^{-1} \cdot s^{-1}$ from 5.9×10^{-6} $cm^{-1} \cdot s^{-1}$ for the period between 8 and 24 hours. These results indicate that the UV-induced reactions of the sample matrix slowed down at this stage, and the elimination of organic pollutants became dominant. Better compliance with zero order assumption for matrix attenuation dynamic was found at the time after 8 hours with an R^2 of 0.96. However, the R^2 value for the first 8 hours' period was only 0.828, indicating a significant limitation raised by assuming the matrix as a unique species. The quantum yields of target pollutants in wastewater (ϕ_W) are determined by the developed

kinetic model and listed in **Table 4.3**. Since the dynamic of light attenuation had a critical point at 8 hours, the treatment process was divided into two periods to conduct simulation (**Figure 4.9**). All the calculated R^2 for the model simulation regarding different PAHs were above 0.97 for the period after 8 hours (by treating the point at 8 hours as the start point).

However, in **Figure 4.9**, there was a significant increase in concentration for PHE at the first 4 hours. Since the photolysis can generate radicals, in the condition of lack oxygen, there could be considerable photosynthesis reactions in this process. Evidence for this mechanism was that there was a layer of oil film form after a long-term of irradiation, and the color became much darker than the initial since more large insoluble molecules were generated. Similar phenomena were also observed for FLO, NAP, and ANT. The photosynthesis of PAHs from certain species in produced water matrix can be a major reason for the increase of concentration (Menor‐Salván *et al.*, 2008). Virtually, we test all the USEPA priority 16 PAHs. This effect can be enlarged for the PAHs larger than 3-rings, and the peak increase can reach to 200% since the concentration is lower and the source can be more abundant. ACY was the only PAH found to have no significant increase in concentration. NAP was found to have less difference between the experimental data and model predicted value since its higher concentration and solubility can reduce the effects of interference.

Since releasing and formation of target PAHs significantly interfered the investigation of PAHs' degradation during first 4 hours, only the data between 4 hours to 8 hours was used to calculate the quantum yields for the first 8 hours. The determined R^2 for ACY between observed data and model simulated data of the whole 24 hours was 0.99 whereas

the R^2 of the first order kinetic model was only 0.71. The model fitted quantum yields for all the PAHs before and after the critical point ($\phi_{W,0-8}$; $\phi_{W,8-24}$) were calculated, and the results are listed in **Table 4.3**. These values are also compared with the quantum yield values in deionized water (ϕ_D) (**Figure 4.10**). According to these results, the quantum yields were virtually increased by the sample matrix indicating that the secondary process involved ^{3}DOM* significantly enhanced the photolysis (Vione *et al.*, 2015). The more reactive matrix in first 8 hours may lead to higher concentration of ^{3}DOM* so that the quantum yields in the first 8 hours were much higher than those values between 8 and 24 hours. ANT was the only PAH observed to have no significant decrease of quantum yield after critical points which may be caused by its high degradability and light absorptivity (Kahan *et al.*, 2010). Since in the original developed kinetic model, quantum yields of targets are treated as constants, the resulted piecewise modeling can be a significant limitation for this model.

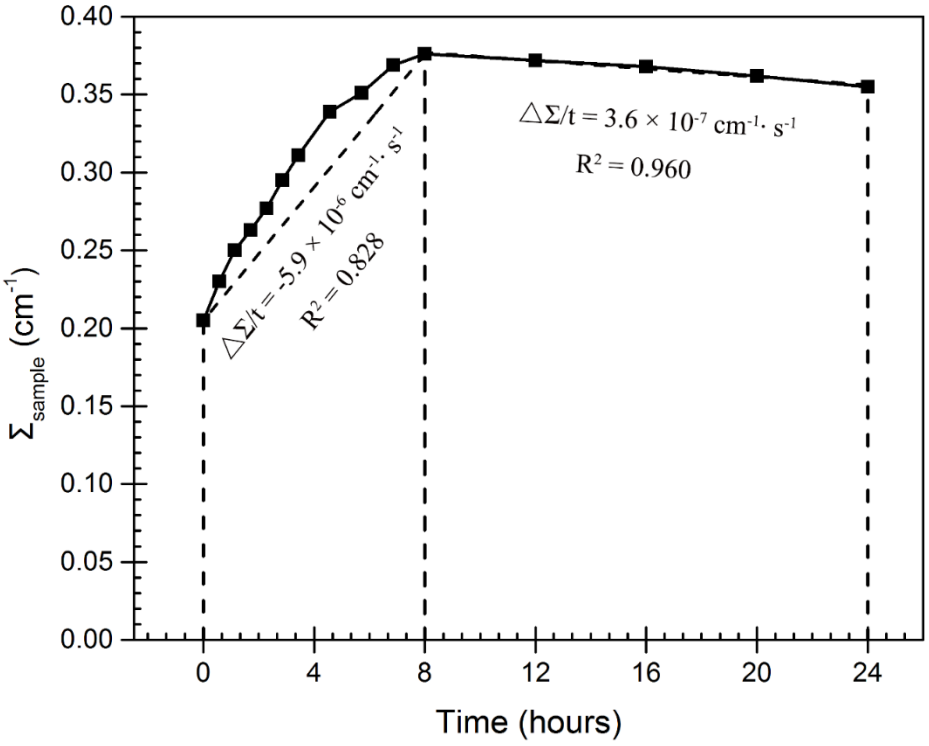


Figure 4.8 Dynamic changing of sample attenuation along with irradiation time

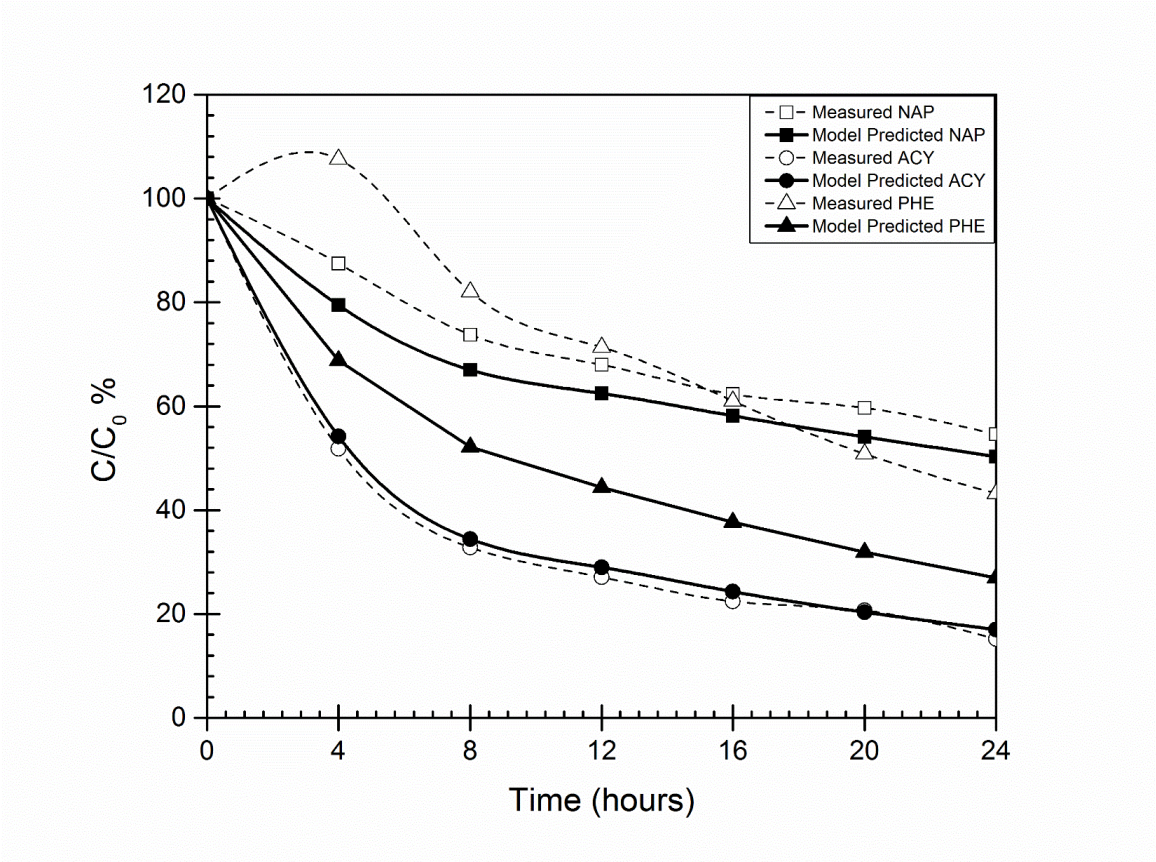


Figure 4.9 Comparison of measured removal rates and model simulation

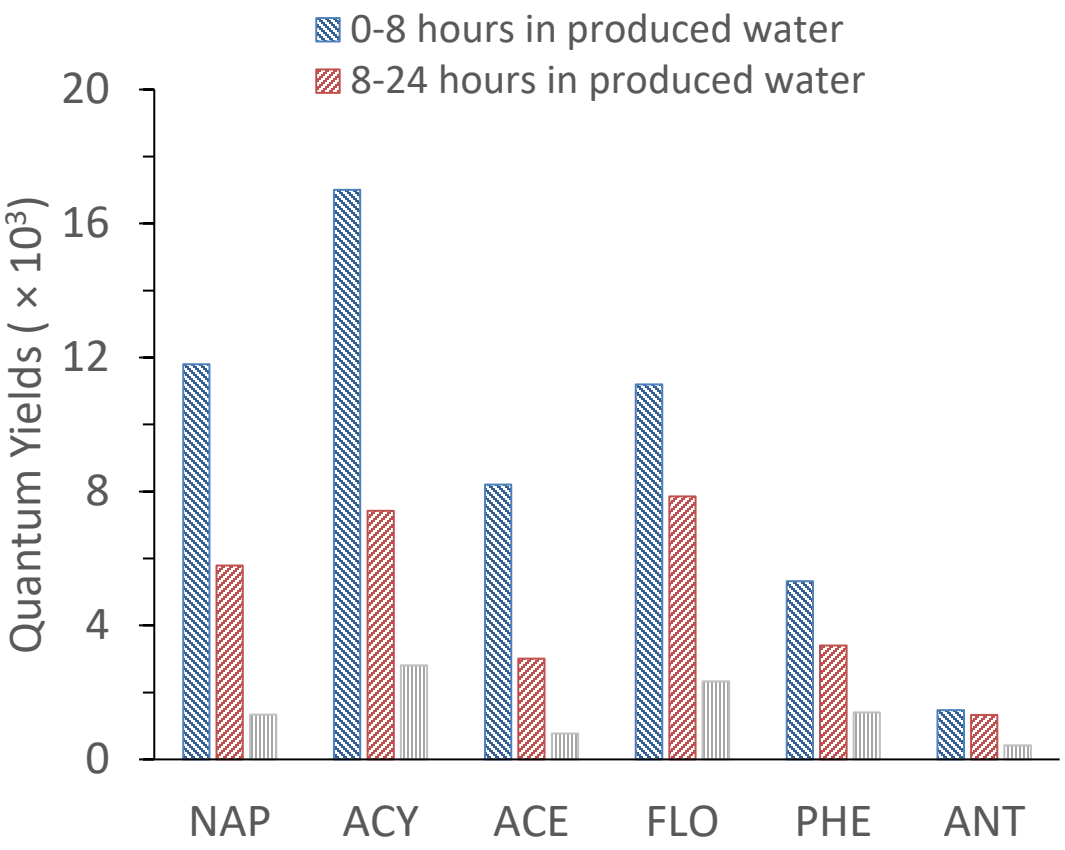


Figure 4.10 Comparison of quantum yields in offshore produced water for different time periods with those in deionized water

Table 4.3 Summary of parameters determined by the developed kinetic model

	Extinction Coefficient	Time	Wastewater Characterization		Model Fitted Parameter	
	ϵ ($M^{-1}\cdot cm^{-1}$)	$t_{initial}$-t_{end} (hours)	Initial Attenuation Coefficient μ_0 (cm^{-1})	Hypothetic Matrix Quantum Yield ϕ_M	Quantum Yield in Wastewater ϕ_W	Quantum Yield Correlation Factor θ
NAP	3.4×10^3	0-8 8-24	0.205 0.376	-1.78×10^{-2} 1.10×10^{-3}	1.18×10^{-2} 5.79×10^{-3}	3.91
ACY	6.3×10^3	0-8 8-24	0.205 0.376	-9.66×10^{-3} 5.93×10^{-4}	1.70×10^{-2} 7.42×10^{-3}	3.37
ACE	5.5×10^3	0-8 8-24	0.205 0.376	-1.10×10^{-2} 6.78×10^{-4}	8.21×10^{-3} 3.01×10^{-3}	2.78
FLO	6.8×10^3	0-8 8-24	0.205 0.376	-8.99×10^{-3} 5.52×10^{-4}	1.12×10^{-2} 7.85×10^{-3}	7.85
PHE	1.2×10^4	0-8 8-24	0.205 0.376	-4.96×10^{-3} 3.04×10^{-4}	5.32×10^{-3} 3.40×10^{-3}	6.24
ANT	7.8×10^4	0-8 8-24	0.205 0.376	-7.77×10^{-4} 4.77×10^{-5}	1.47×10^{-3} 1.33×10^{-3}	27.88

4.3.5 Finite-Element Method (FEM) Semi-empirical Model and Validation

In the case of offshore produced water, the dynamic changing of sample's attenuation coefficient did not follow zero-order which led to errors with model's assumptions. On the other hand, the quantum yields of target pollutants showed none constant. Therefore, a finite-element method (FEM) concept and an empirical factor were applied to transform the developed kinetic model. By transforming the kinetic equation, the following relationship between removal rate and attenuation coefficient can be obtained:

$$\frac{C_{PAH(t)}}{C_{PAH,0}} = (1 + \frac{\Delta\mu_{sample}}{\mu_{sample,0}})^{-\frac{\phi_{PAH}\epsilon_{PAH}I_0}{\Delta\mu_{sample}}t} \quad (1)$$

By dividing the time into a number (n) of same finite time fragments (t_i, t_{i+1}), the assumption of zero order kinetic can be approximated when n is large enough. Assume the attenuation coefficient μ_{sample} equals to a fixed function of t as $\mu(t)$, the removal rate in single time fragment can be calculated by:

$$R_{(t_i,t_{i+1})} = \frac{C_{PAH,t_{i+1}}}{C_{PAH,t_i}} = [1 + \frac{\mu_{(t_{i+1})}-\mu_{(t_i)}}{\mu_{(t_i)}}]^{-\frac{\phi_{PAH}\epsilon_{PAH}I_0}{\mu_{(t_{i+1})}-\mu_{(t_i)}}(t_{i+1}-t_i)} = [\frac{\mu_{(t_{i+1})}}{\mu_{(t_i)}}]^{-\frac{\phi_{PAH}\epsilon_{PAH}I_0}{\mu_{(t_{i+1})}-\mu_{(t_i)}}(t_{i+1}-t_i)} \quad (2)$$

Therefore, the total removal rate during time (t_0=0, t_n=t) can be obtained by:

$$\frac{C_{PAH,t}}{C_{PAH,0}} = \prod_{i=0}^{n}[\frac{\mu_{(t_{i+1})}}{\mu_{(t_i)}}]^{-\frac{\phi_{PAH}\epsilon_{PAH}I_0}{\mu_{(t_{i+1})}-\mu_{(t_i)}}(t_{i+1}-t_i)} \quad (3)$$

In this case, the attenuation coefficient was fitted by the function below with R^2 of 0.99 with the data shown in **Figure 4.8**:

$$\mu(t) = 0.4564e^{-3\times10^{-6}t} - 0.2533e^{-5.567\times10^{-5}t}$$

Since the increased ϕ_A is contributed by the production of ^{3}DOM*, there should be a

correlation between the ϕ_{PAH} and ϕ_M. By an analysis of the data of the ϕ_M and ϕ_{PAH} in **Table 4.3**, following correlation was proposed:

$$\phi_{PAH} = \alpha|\phi_M|^{\frac{1}{\theta}} \quad (4)$$

Where α is a constant; and the values of θ were determined by:

$$\theta = \frac{\ln\left(\left|\frac{\phi_{M,0-8}}{\phi_{M,8-24}}\right|\right)}{\ln\left(\frac{\phi_{W,0-8}}{\phi_{W,8-24}}\right)} \quad (5)$$

The values of θ were calculated and listed in **Table 4.3**. By substituting the equation 4 and the definition ϕ_M (equation 24 in section 4.2.1), the equation 3 can be transformed to:

$$\frac{C_{PAH,t}}{C_{PAH,0}} = \prod_{i=0}^{n}\left[\frac{\mu_{(t_{i+1})}}{\mu_{(t_i)}}\right]^{-\frac{\gamma|\mu_{(t_{i+1})}-\mu_{(t_i)}|^{\frac{1}{\theta}}}{\mu_{(t_{i+1})}-\mu_{(t_i)}}(t_{i+1}-t_i)} \quad (6)$$

$$\text{Where } \gamma = a \cdot (\epsilon_{PAH} I_0)^{(1-\frac{1}{\theta})} \quad (7)$$

Where γ is defined as the reaction correlation constant and θ is defined as the quantum yield correlation factor. **Figure 4.11** shows the comparison of the developed FEM model simulation, first order kinetic simulation and observed degradation for ACY in offshore produced water. The models were calibrated with ACY's removal rate at 24 hours. The results indicate that significant advantage of the developed semi-empirical FEM model compared to the first order kinetic model. The developed semi-empirical FEM model was also validated by the data for all the other PAHs. The results are summarized in **Figure 4.12**. The overall R^2 of the model is equal to 0.8468. However, the developed model mostly performed underestimations. It is because of the interference raised by formation and releasing of PAHs from sample matrix during photolysis. The points at 4 hours, of which the concentrations of PAHs were observed to be increased, showed the largest errors. These

may interfere the model's simulation especially when target's concentration is low. Also, since the relationships between the operational parameters (irradiance intensity, temperature), the water properties (salinity, DOC, COD) and the factors in the model (ϕ_{PAH}, ϕ_M) remain unidentified, the developed models recently have difficulties for utilization in system design. However, these models can provide an option with the new concept other than classic first order kinetic. In a fixed condition for which the parameters are measured and calculated with experiments, these models can show good performance for simulation and kinetic analysis. They also provide a foundation for the development of modeling trace organic pollutants (including emerging contaminants) in wastewater with high light attenuation.

4.4 Summary

Direct photolysis is an important process for the degradation of organic pollutants such as polycyclic aromatic hydrocarbons (PAHs). The removal of trace organic pollutants in high salinity wastewaters such as offshore produced water usually show complicated mechanisms. than those in cleaner waters. This impact is mainly caused by complicated chemical constitutions of produced water. In such process, dynamic changes of sample's light attenuation may challenge the modeling of degradation. In this study, a kinetic model and a semi-empirical model were developed to tackle these challenges by introducing light screening dynamics. According to the results of validation in potassium iodide solution, the improvement of simulative performance was confirmed. In offshore produced water,

unlikely to the restarted degradation rates, the quantum yields of PAHs were higher than those in deionized water, indicating that the chemical species in produced water can lead to significant photo-synthetization effects. However, the developed kinetic model still has significant limitations since the PAHs' quantum yields are not constant and the light screening dynamics are more complicated in offshore produced water. Also, the radical synthesis effect may also significantly affect the concentration of PAHs. Therefore, further studies focusing on understanding and simulating these mechanisms are demanded.

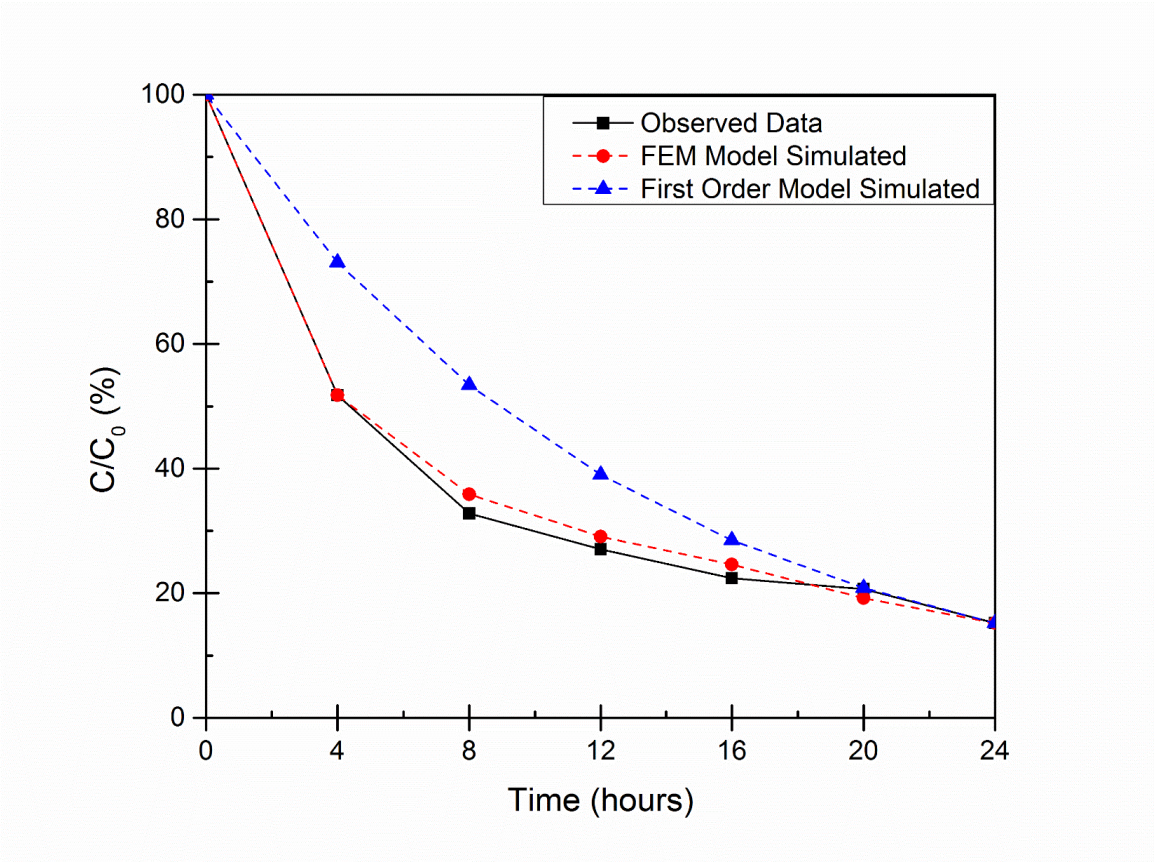


Figure 4.11 Comparison of model simulation, first order kinetic model simulation and observed degradation of ACY during the UV photolysis of offshore produced water

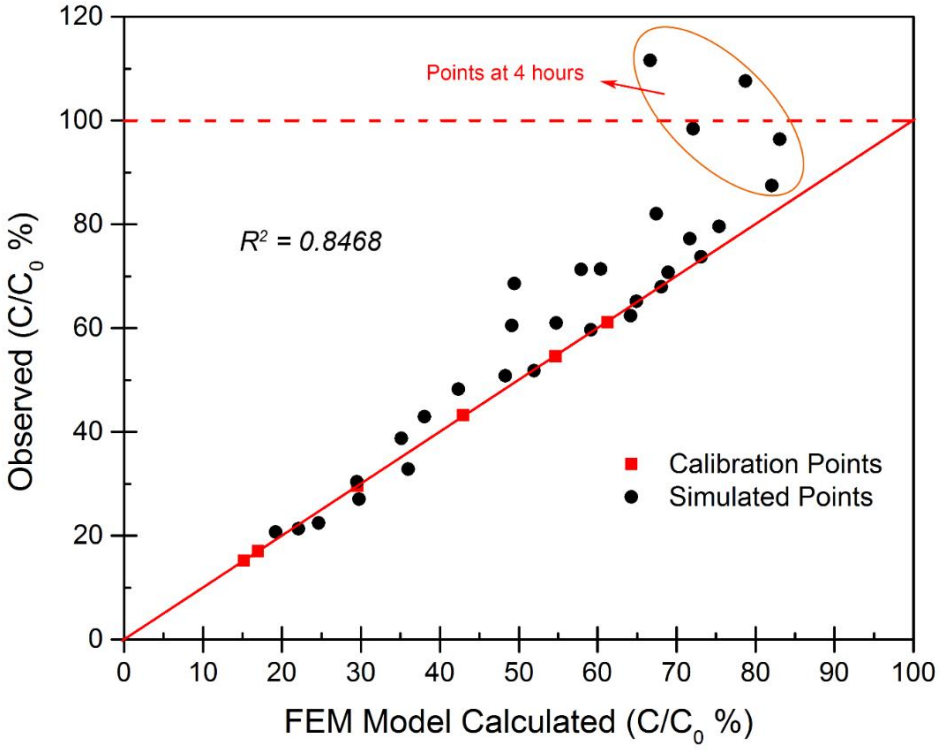


Figure 4.12 FEM model validation
($\gamma_{NAP} = 7.3 \times 10^{-5}$; $\gamma_{ACY} = 3.9 \times 10^{-4}$; $\gamma_{ACE} = 2.3 \times 10^{-4}$; $\gamma_{FLO} = 2.7 \times 10^{-5}$; $\gamma_{PHE} = 2.9 \times 10^{-5}$; $\gamma_{NAP} = 1.15 \times 10^{-5}$)

CHAPTER 5 REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS IN OFFSHORE PRODUCED WATER BY OZONE AND UV/OZONE

5.1 Background

The removal of dispersed and dissolved hydrocarbons from offshore produced water (after gravity separator and flotation) has been challenging in the environmental impact management. Current onsite produced water treatment is mainly dependent upon physical separation of the bulk of oil from the water to meet the regulatory standards (e.g., hydrocyclone and air floatation) (Jing *et al.*, 2014a; Jing *et al.*, 2014b). However, they have low efficiency in the removal of the dissolved organic compounds that make a significant contribution to the toxicity of the produced water (Chen *et al.*, 2010). It is possible via many techniques such as biofiltration, biodegradation, phytoremediation, photocatalysis (Liu *et al.*, 2014) and adsorption with subsequent biological treatment (Haritash and Kaushik, 2009; Souza Duarte *et al.*, 2011). However, most of them have various limitations that must be considered as onsite treatment technologies for installation on the production platforms or vessels particularly in harsh marine environments (Hawboldt *et al.*, 2010). On-site treatment of offshore produced water is desirable due to the low shipping and handling costs, as well as reduced health, safety, and environmental concerns. In offshore operations, weight and space are the most severe constraints. The cold temperatures, fragile ecosystems, and requirement in some cases of unmanned operations add further complexity to produced water treatment in cold oceans and harsh environments (Jing *et al.*, 2012).

As indicated above, there are limited studies on produced water. Although these studies have shown that ozonation has great potential in decomposing dissolved organic compounds (Wang *et al.*, 2013; Klamerth *et al.*, 2015), most of them focus on a single or a limited number of compounds, and the complexity of the produced water composition is

not considered. Also, the reaction dynamics of the combination of ozone and ultraviolet are unclear, and questions regarding if the process is fundamentally different from either ozone or UV treatment alone remain unanswered. Photo-oxidation of hydrocarbons has sometimes been documented to increase toxicity (Casini *et al.*, 2006). Further research is in high demand to investigate the treatment efficiency for produced water and the associated risks and toxicity effects of photo-oxidation in combination or on their own.

5.2 Methodology

5.2.1 Materials

The 16-component PAHs standard mix was supplied by Agilent® Technologies Inc. (p/n 8500-6035) and used in the experiments to avoid any possible impact on the analysis of degradation mechanism. 1ml vial of 16 PAHs standard with a concentration of 500µg/ml was purchased from VWR®. The PAH stock solution had a nominal concentration of 500 µg/ml naphthalene (NAP); acenaphthylene (ACY); acenaphthene (ACE); fluorine (FLO); phenanthrene (PHE); anthracene (ANT); fluoranthene (FLA); pyrene (PYR); chrysene (CHR); benz [a] anthracene (BaA); benzo [b] fluoranthene (BbF); benzo [k] fluoranthene (BkF); benzo [a] pyrene (BaP); dibenzo [a, h] anthracene (DahA); indeno [1,2,3-cd] pyrene (IcdP); benzo [g, h, i] perylene (BghiP). The ultra-high purity water and solvents including dichloromethane and acetone were of reagent grade or equivalent quality purchased from VWR® International (Mississauga, Ontario, Canada) and Fisher Scientific (Ottawa, Ontario, Canada). The spiking stock was made by diluting the purchased standards into 5µg/ml with

acetone.

The deuterated PAHs with high purity were used as surrogates: NAP-d_8 (99%), ACE-d_{10}, PHE-d_{10} (99%) and benzo [a] DahA-d_{12} which were obtained from Cambridge Isotopes Labs (St. Leonard, Quebec, Canada) and C/D/N Isotopes Inc. (Pointe-Claire, Quebec, Canada), respectively. P-Terphenyl-d_{14} (2,000 µg/ml) purchased from VWR International (Mississauga, Ontario, Canada) was used as internal standards (IS). Sodium chloride (NaCl) was also obtained from VWR International (Mississauga, Ont., Canada). The solvents, including ultra-high purity water, were of reagent grade or equivalent quality purchased from VWR International (Mississauga, Ontario, Canada) and Fisher Scientific (Ottawa, Ontario, Canada).

Offshore produced water samples were collected from Atlantic Canada. Right after the collection from the sampling sites, the water was bottled in an acid washed Nalgene® high-density polyethylene (HDPE) jerrican (10 L) and then placed in a cooler. Ice packs were also used in the cooler to cool down the produced water immediately. It also assists to maintain the low temperature and keeps the steady position to avoid swash of produced water. When entering the lab, the produced water sample was placed in a 4 ^{o}C fridge. The darkness condition inside the refrigerator was maintained to avoid light irradiation of the compounds in the samples. The collected produced water samples had high salinity and organic loadings. Also, the concentrations of most PAHs were below the LODs of the method. Thus, this sample was spiked with 16 PAHs (0.2 ppb) to carry out the kinetic study within sample matrix to identify the interactions between PAHs and the water substrate. The preparation of spiked offshore produced water sample is as follows. 1 L sample was poured into a beaker from the jerrican, and 100 µL spiking stock was added. The water was

mixed for 30 minutes by the stirrer to achieve normal temperature.

5.2.2 Facilities

Column Reactor

Three 1-L glass bubble columns (40 cm Long x 7.5 cm Diameter) were designed and fabricated in this project (**Figure 5.1**) to test ozonation technology for treating offshore produced water. The sample inlet is at the top of the column, while the sample outlet is located at the bottom of the column. A switch is used to control the sample flow. The ozone inlet is located at 35 cm from the top beside the column. Near the bottom of the column, a diffuser is located, through which ozone is introduced, and bubble size is changed by using different diffusers (refer to **Table 5.1**). There is a silicon stopper to seal the reaction chamber at the top of the column, on which the UV irradiation protector (quartz tube) and ozone outlet tube are fixed. An ozone destructor was connected to the ozone outlet to prevent the residual ozone entering the ambient environment.

Table 5.1 Calibrated parameters for different diffusers

Diffuser	Pore Size, µm	Mean Bubble Diameter, µm
ASTM-A	500	1114
ASTM-B	100 - 170	590
ASTM-C	20 - 70	104

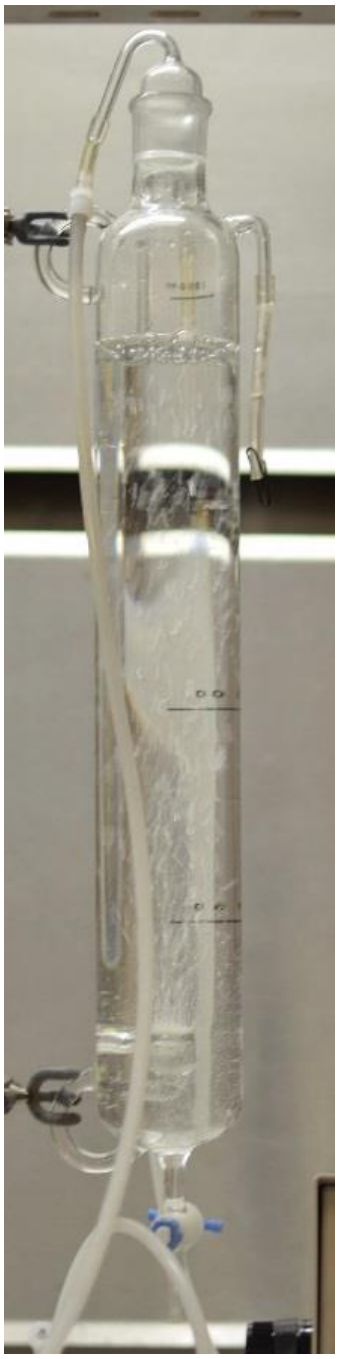


Figure 5.1 The bubble column reactor

Ozone Generation

The ozone generation system consists of an oxygen gas cylinder and an ozone generator. A gas regulator on the cylinder is used to control the oxygen flow inside the column. The ozone generator can be used to generate ozone and monitor or control the ozone concentration in the oxygen flow.

While for the developed UV-enhanced ozonation (UVO) system used for produced water treatment, as depicted in the schematic diagram (**Figure 5.2**), there are five major components. The photo of this scheme is shown in **Figure 5.3**. The components are:

Column Reactor: the column used in ozonation experiments were directly employed in the UV-enhanced ozonation system;

Monitoring Chamber: the monitoring chamber is designed for the sampling and monitoring of the treated sample. This chamber was connected to sample inlet and outlet of the column with tubes. Besides the inlet and outlet, the 300-ml sampling chamber has a draining port to collect the samples for GC-MS analysis. The dissolved ozone in the treated water was measured by a dissolved ozone sensor. The temperature of the water is monitored by sensor inside the chamber;

UV Irradiation Module: the UV irradiation unit consists of a power supply and a UV lamp with maximum 4 mW/cm^2 irradiation intensity. The irradiation intensity can be adjusted by changing the output energy of the power supply. The lamp is isolated by a quartz tube and immersed in the produced water sample in the column;

Ozone Generation Module: the ozone is provided by the same generation module as those in ozonation experiments;

Pumping System: the last component is a pumping system to maintain and control the

continuous sample flow between the reaction column and sampling chamber. These two pumps can adjust the water flow rate between the reaction column and monitoring chamber to achieve the trade-off between water consistency and increased pressure the reaction column.

Bubble Size Measurement

The bubble size was measured during the ozonation experiment to evaluate the associated impact on the treatment. The bubble plume was first captured by a high-resolution digital SLR camera (Nikon, D3200) using the high-speed mode. As a reference, a rule was marked on the outside wall of the bubble column enabling the determination of bubble size. The quality of the captured images was high (22.4 Megapixels). The images obtained were analyzed using the Image-Pro® software to quantify the bubble size. The color and contrast could be adjusted using the software to distinguish the bubbles from the ambient water to count the number of bubbles and calculate the size of each bubble. Through statistical analysis, the bubble size distribution was generated (**Figure 5.4**).

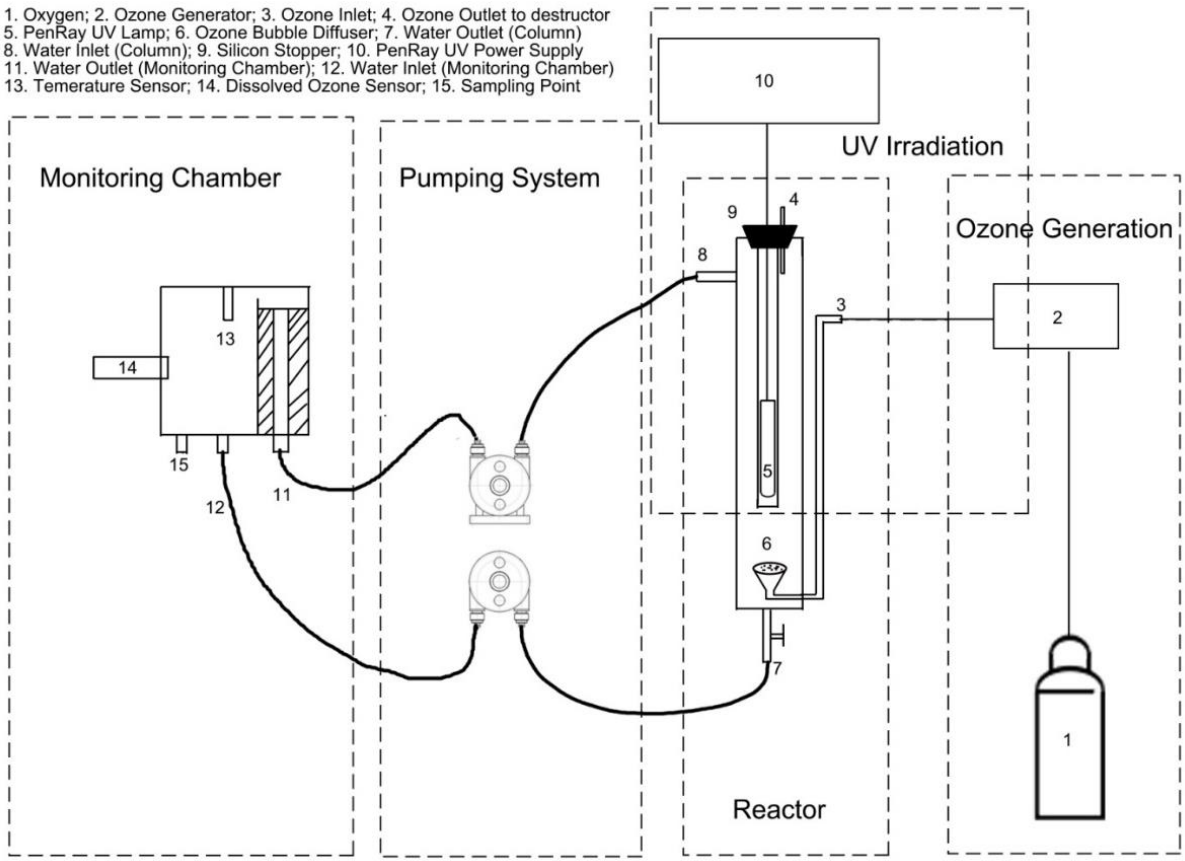


Figure 5.2 Scheme of UV/Ozone system

Figure 5.3 Setup of developed UV/Ozone system

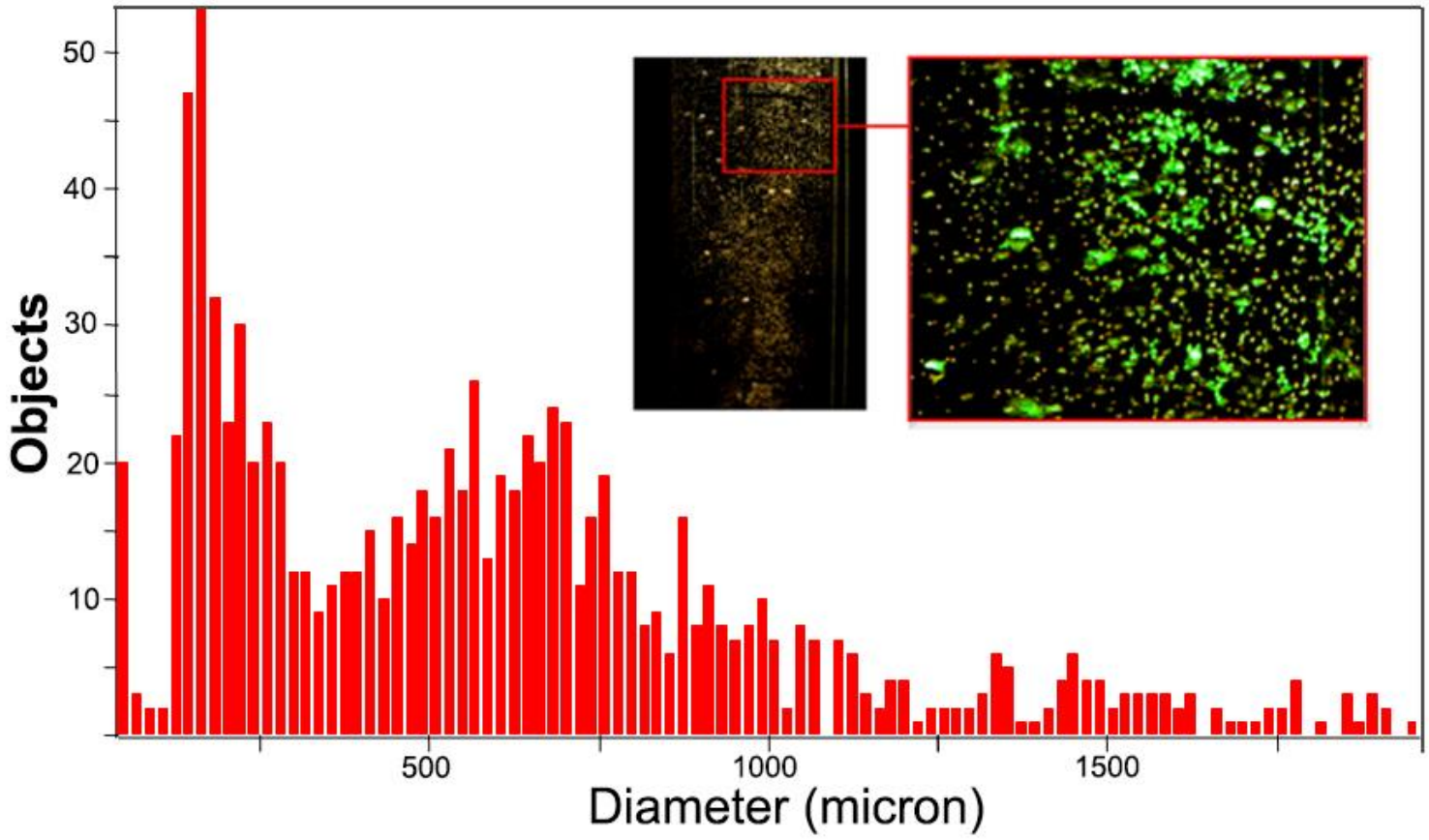


Figure 5.4 Bubble analysis by ImagePro® software

Element Analysis

Element analysis of produced water samples was conducted by the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in the Earth Resources Research and Analysis Facility (TERRA) of Memorial University for element analysis. Sample bottles were cleaned beforehand by soaking in 2 N HNO_3 overnight, then rinsed with pure water and air-dried in a clean air fume hood. The produced water samples were filtered (0.45 micron) and acidified. For proper acidification, 25 ml 8 N HNO_3 acid was added to a one-liter water sample. Acidification ensures that metals are retained in solution.

Dissolved Organic Carbon (DOC) Analysis

The TOC-5000A total organic carbon (TOC) analyzer (Shimadzu®, Japan) was used for the measurement of the DOC.

Toxicity Analysis

Microtox® is an acute toxicity test using the marine luminescent bacterium *Vibrio fischeri* (formerly known as Photobacterium phosphoreum). This bacterium emits light because of normal metabolic processes. A reduction in luminescent ability during exposure to contaminants or pollutants is taken as a measure of toxicity.

A Microtox® Model 500 analyzer (Microbics Corp., Carlsbad, CA, USA) was used to perform the toxicity testing. The freeze-dried bacteria (approx. 10^6 cells), reconstruction solution, diluent (2% NaCl) and adjustment solution (non-toxic 22% sodium chloride dilution) were obtained from Microbics Corporation (Carlsbad, CA, USA).

Biodegradability Analysis

An eight-position, Model AER-208 Respirometer (Challenge Environmental Systems, Fayetteville, AR) equipped with 500-mL reaction vessels was used to measure oxygen uptake rate (OUR) and analyze the impact of ozonation on biodegradability. Each reaction vessel was filled with 500 mL of mixed liquor sample containing a constant biomass concentration (2,000 mg VSS/L or 2,840 mg COD/L calculated using the conversion factor 1.42 mg COD/mg VSS). Using AER-208, up to 8 samples could be tested simultaneously.

5.2.3 Experimental Methods

The scheme of the lab experiments in this research is shown in **Figure 5.5**. The sampled produced water was spiked with 16 PAHs since the concentrations of most PAHs were near or below the detection limit (2 ng/L). For understanding and evaluating the effect of different parameters, the adjusted operational condition was tested, and the treated samples were processed with developed analytical methods. The obtained data were analyzed for model development and kinetic discovery. Meanwhile, the toxicity of the treated samples will also be examined to confirm the performance of the treatment. That kinetics and toxicity will help to value selection of parameters for conduction the next round of treatment experiment.

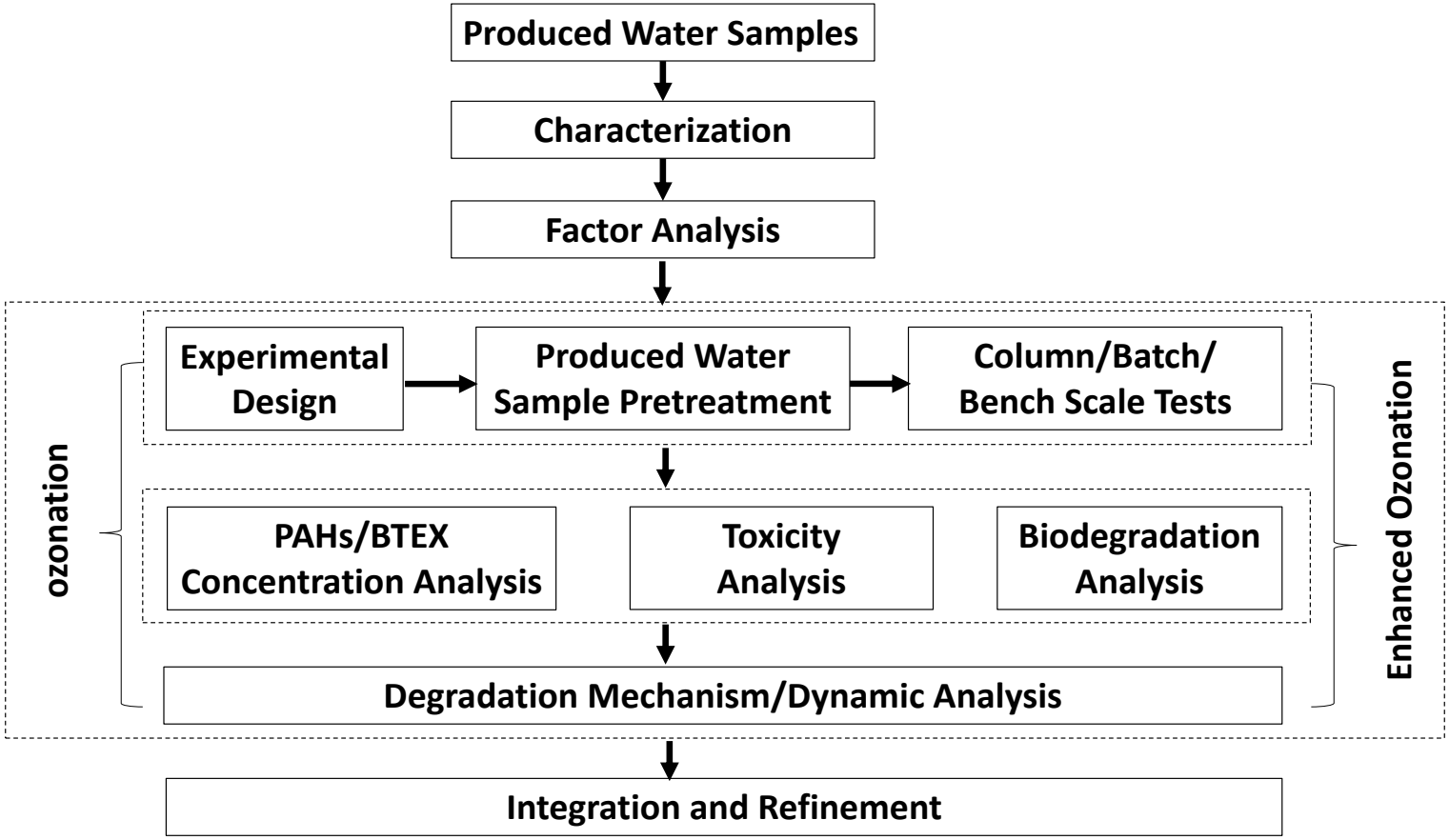


Figure 5.5 Scheme of produced water ozonation experiment

Ozonation Reactions and Control Factors

Oxidation of organic pollutants in water by ozonation is usually initiated by two different pathways: 1) the direct reaction with ozone molecules; 2) the reaction with hydroxyl radicals which are generated by the chain reaction of ozone with water. Therefore, the key control factors related to both reactions can cause significant effects on the efficiency of the oxidation process:

a. Bubble size

The reaction of aqueous pollutant and gas phase ozone can be expressed by equation 1.

$$O_3(g) + M(aq) \rightarrow P(aq) \qquad (1)$$

The reaction rate can be determined by

$$-\frac{d[M]}{dt} = ak_p [M]_{aq} [O_3]_g \qquad (2)$$

Where a is the interfacial area. On the other hand, the mass transfer of ozone from bubble into water also depends on the interfacial area, which is demonstrated by the following equation:

$$\frac{d[O_3]_L}{dt} = ak_L \left([O_3]_L^* - [O_3]_L \right) \qquad (3)$$

Therefore, the interfacial area is impacting interphase and aqueous phase reaction of ozone intensively.

The bubble size is the major factor that controlling the interfacial area. For instance, a system has gas flow of Q and bubble retention time of t_r, by assuming the bubble radius of r, the interfacial area can be determined by

$$a = \frac{Qt_r}{\frac{4}{3}\pi r^3} 4\pi r^2 = \frac{3Qt_r}{r} \qquad (4)$$

From the above equation, smaller bubble size can lead to a larger interfacial area.

b. Ozone dose

As the key reactant of ozonolysis, the removal of contaminants highly depends on the concentration of ozone. In this research, four levels of gas phase ozone concentration (5 ppm, 10 ppm, 20 ppm and 40 ppm) with the constant gas flow of 250 ml/min were examined to validate the effect of ozone dose. The adjustment of ozone generator's power output can obtain the variance of this parameter.

c. pH

pH value indicates the $[H]^+$ and $[OH]^-$ in the water. Higher pH values refer to the higher concentration of OH^- in water. The chain reaction for hydroxyl radical's generation in water highly depends on the concentration of OH^- since it is initiated by equation 7.

$$O_3 + OH^- \rightarrow O_2^- \cdot + HO_2 \cdot \qquad (7)$$

The reaction rate constant is 70 $M^{-1}s^{-1}$. Since the rate constant is relative low comparing to some other high concentration components in offshore produced water matrix (I^-, Br^-, olefins), only the increased concentration of OH^- can significant generation hydroxyl radicals at the initial stage. On the other hands, some chemical species such as amines, phenols, and olefinic acids also have pH-dependent reaction constant for direct ozone reaction. To examine the importance of pH and justify the direct ozone reaction and hydroxyl initiated reaction, three different pH values (3, 7 & 10) were applied. The different pH values were achieved by the addition of hydrochloric acid and sodium hydroxide.

d. Temperature

The chemical reaction constants (k) usually depend on the temperature. In produced water, there is also a significant content of volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC). These chemical species can be brought out by ozone gas flow of which the efficiencies are controlled by their Henry's Law Constants (He) which is dependent on the temperature. To examine the effect of temperature, three temperature levels (40 ºC, 50 ºC, 60 ºC) were applied based on produced water working condition. A special column with water bath outside the column body was used. The different temperature levels were achieved by a boiling pot of a rotary evaporation device.

5.3 Results and Discussion

5.3.1 Offshore Produced Water Characterization

Organics

Two sets of samples collected from the same well but in different date were thoroughly analyzed for characterization purpose, and the results were discussed here. One set obtained on August 16th, was labeled as OPW I; and the other set obtained on June 4th, was labeled as OPW II.

The organic matters in produced water were analyzed mainly by GC-MS as per the analysis methods discussed in chapter 3. The DOC analysis was supplemented. The DOC values of produced water varied from 170-220 mg/L. The organic components in produced water mainly included hydrocarbons (includes PAHs and BTEX), organic acids and

phenols. The average concentrations of 16 EPA priority PAHs are listed in **Table 5.2**. Naphthalene showed the highest concentration in produced water samples (i.e., around 20 μg/L). Trace levels of fluorene, phenanthrene, pyrene, chrysene, benzo [b] fluoranthene, benzo [a] pyrene and benzo[g,h,i]perylene were also detected.

The TIC chromatogram (**Figure 5.6**) demonstrated the major organic components in offshore produced water, which were phenol and its alkyl homologs, aromatic hydrocarbons and aliphatic hydrocarbons. As labeled in Figure **5.6**, C_1-C_3 Phenols were dominated in the retention time before 15 minutes. After 15 minutes, alkanes were eluted following the increase of carbon atoms.

Inorganics

The salinity of produced water was around 50 ppt, which was higher than seawater which is around 23-35 ppt). The pH was around 7. The non-metal elements are tabulated in **Table 5.3**. Halogen elements are predominant in produced water.

Metals

As shown in **Table 5.4**, strontium, lithium, iron and zinc had the highest concentrations in both produced water samples. All of them had a concentration greater than 1 mg/L. Besides calcium and manganese, strontium showed a leading role in term of concentration (~14 mg/L). Compared with those in seawater, the concentrations of iron, lead, manganese, rubidium, strontium, barium and zinc were much higher in produced water.

Table 5.2 The concentrations of US EPA 16 PAHs in offshore produced water

PAHs	Abbreviation	OPW I (µg/L)	OPW II (µg/L)
Naphthalene	NAP	20.24	20.04
Acenaphthylene	ACY	< LOD	< LOD
Acenaphthene	ACE	< LOD	0.081
Fluorene	FLO	0.11	0.26
Phenanthrene	PHE	0.13	0.54
Anthrancene	ANT	< LOD	< LOD
Fluoranthene	FLA	< LOD	< LOD
Pyrene	PYR	< LOD	0.04
Benzo [a] anthrancene	BaA	< LOD	< LOD
Chrysene	CHR	< LOD	0.24
Benzo [b] fluoranthene	BbF	0.03	0.06
Benzo [k] fluoranthene	BkF	< LOD	< LOD
Benzo [a] pyrene	BaP	0.04	< LOD
Indeno [1,2,3-cd] pyrene	IcdP	< LOD	< LOD
Dibenzo [a,h] anthracene	DahA	< LOD	< LOD
Benzo [g,h,i] perylene	BghiP	0.02	0.06

Note: LOD = Limit of Detection

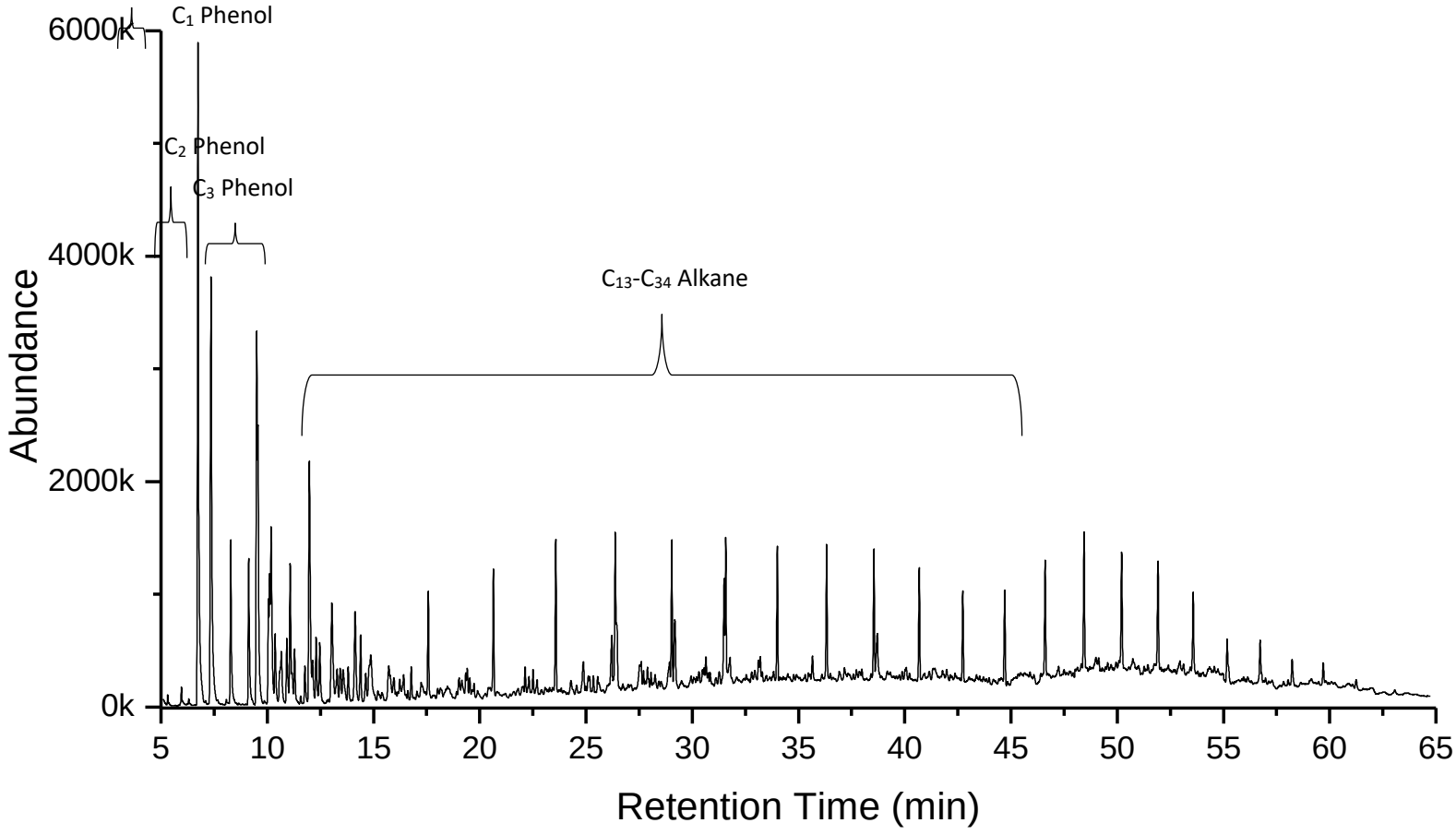


Figure 5.6 GC-MS chromatogram (TIC) of offshore produced water

Table 5.3 Concentrations of concerned inorganics in offshore produced water

Elements	OPW I, ppm	OPW II, ppm
B	15.74	118.77
Si	19.54	19.22
P	< LOD	< LOD
S	633.56	605.45
Cl	16,928.62	17,319.32
Br	89.273	93.56
I	4.957	4.86

Table 5.4 The concentrations of typical metals in offshore produced water

Metal	OPW I ppm	OPW II ppm	Seawater ppm
Li	1.501	1.657	1.800×10^{-1}
Be	<LOD	<LOD	2.700×10^{-7}
Mg	80.151	71.299	1350
Al	3.100×10^{-1}	3.170×10^{-1}	1.080×10^{-3}
Ca	968.881	943.400	400
Ti	<LOD	<LOD	1.197×10^{-5}
V	<LOD	<LOD	1.460×10^{-3}
Cr	<LOD	<LOD	1.180×10^{-4}
Fe	4.081	4.163	4.950×10^{-4}
Mn	8.200×10^{-2}	8.600×10^{-2}	5.300×10^{-4}
Co	<LOD	<LOD	1.767×10^{-5}
Ni	3.400×10^{-2}	3.300×10^{-2}	3.010×10^{-4}
Cu	1.010×10^{-1}	1.120×10^{-1}	2.480×10^{-4}
Zn	8.360×10^{-1}	1.096	2.570×10^{-4}
As	<LOD	<LOD	1.430×10^{-3}
Se	1.400×10^{-2}	1.700×10^{-2}	1.816×10^{-4}
Rb	2.980×10^{-1}	2.990×10^{-1}	1.200×10^{-1}
Sr	13.895	14.196	7.886
Mo	<LOD	<LOD	9.890×10^{-3}

Ag	<LOD	<LOD	3.773×10^{-6}
Cd	<LOD	<LOD	3.100×10^{-5}
Sn	<LOD	<LOD	2.374×10^{-6}
Sb	<LOD	<LOD	1.948×10^{-4}
Cs	2.800×10^{-2}	3.000×10^{-2}	2.924×10^{-4}
Ba	3.490×10^{-1}	3.920×10^{-1}	2.060×10^{-2}
Hg	1.200×10^{-2}	1.200×10^{-2}	2.000×10^{-6}
Pb	2.000×10^{-3}	2.000×10^{-3}	6.000×10^{-6}

5.3.2 General Ozonation of Offshore Produced Water

As shown in **Figure 5.7**, ozonation showed good performance on the removal of organic contaminants in produced water with removal rates ranging from 65.0% to 99.9% during one hour. The chromatograph of treated samples only has some visible peaks for saturated alkanes. In contrast, by purging ozone into 16 PAHs spiked distilled water, the PAHs could be eliminated in less than 1 minute, and the efficiency is much higher. So, the produced water substrate poses a very significant inhibition effect. Produced water usually contains significant amounts of organic and inorganic compounds. Some of them were highly reactive to ozone, such as I^-, ferrous and phenols which can compete for the oxidant with PAHs. Since PAHs have very low concentration, only after the concentration of these chemicals is reduced to a certain level, the PAHs can share a considerable amount of oxidant, then start to be reduced (**Figure 5.8**). **Table 5.5** shows the reaction constants for different PAH species. Compared to the results in **Figure 5.8**, PAHs that have higher reaction constants and ozone showed higher removal rates, indicating that the direct reaction may dominate the process. The concentration increase or slow degradation were also observed. Like the results of photolysis, this might contribute to both the synthesis effect and the destruction of suspended solids and the formation and then disappearance of oil film during the treatment.

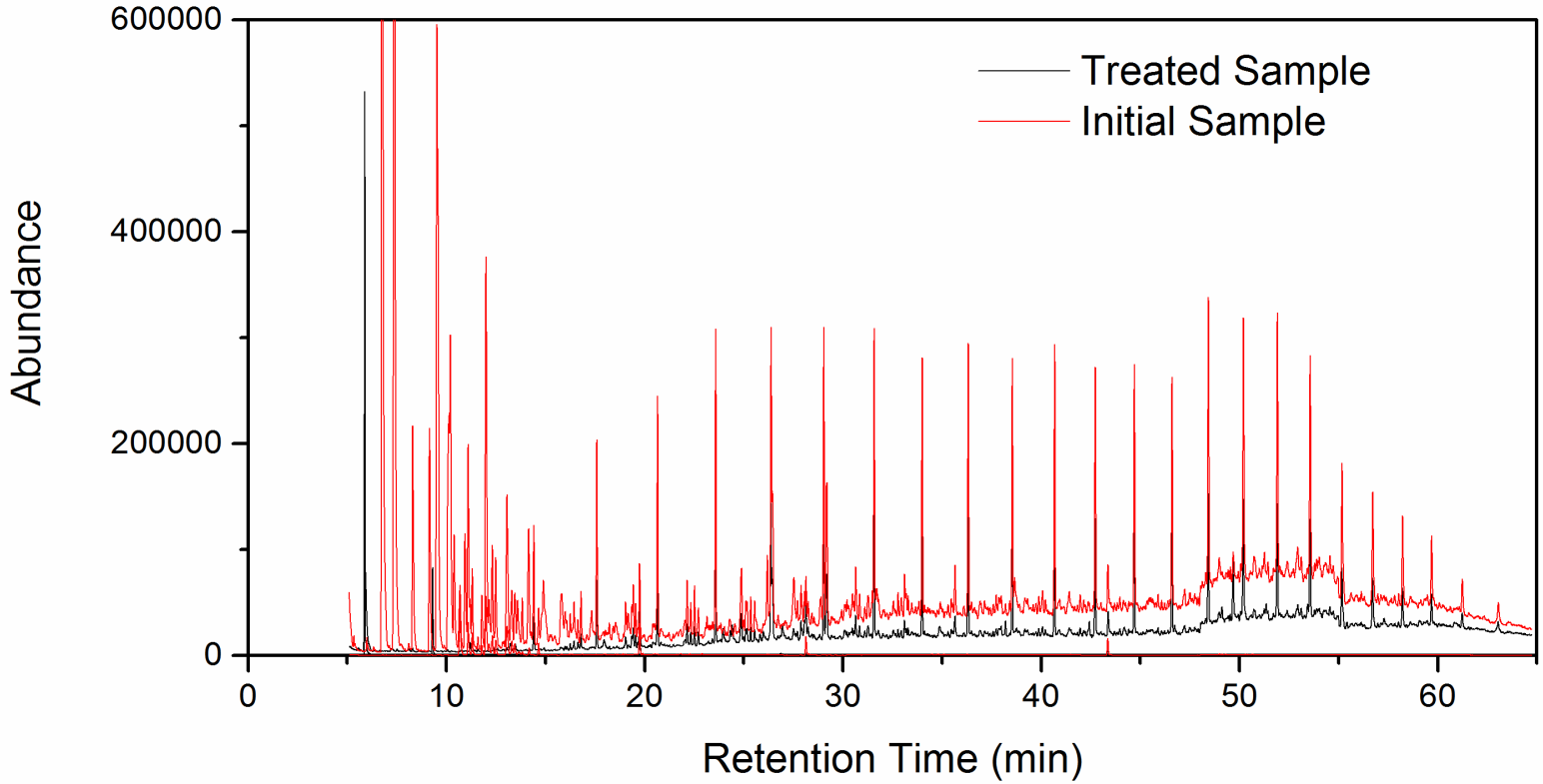


Figure 5.7 Chromatograph of initial/ozonated offshore produced water sample

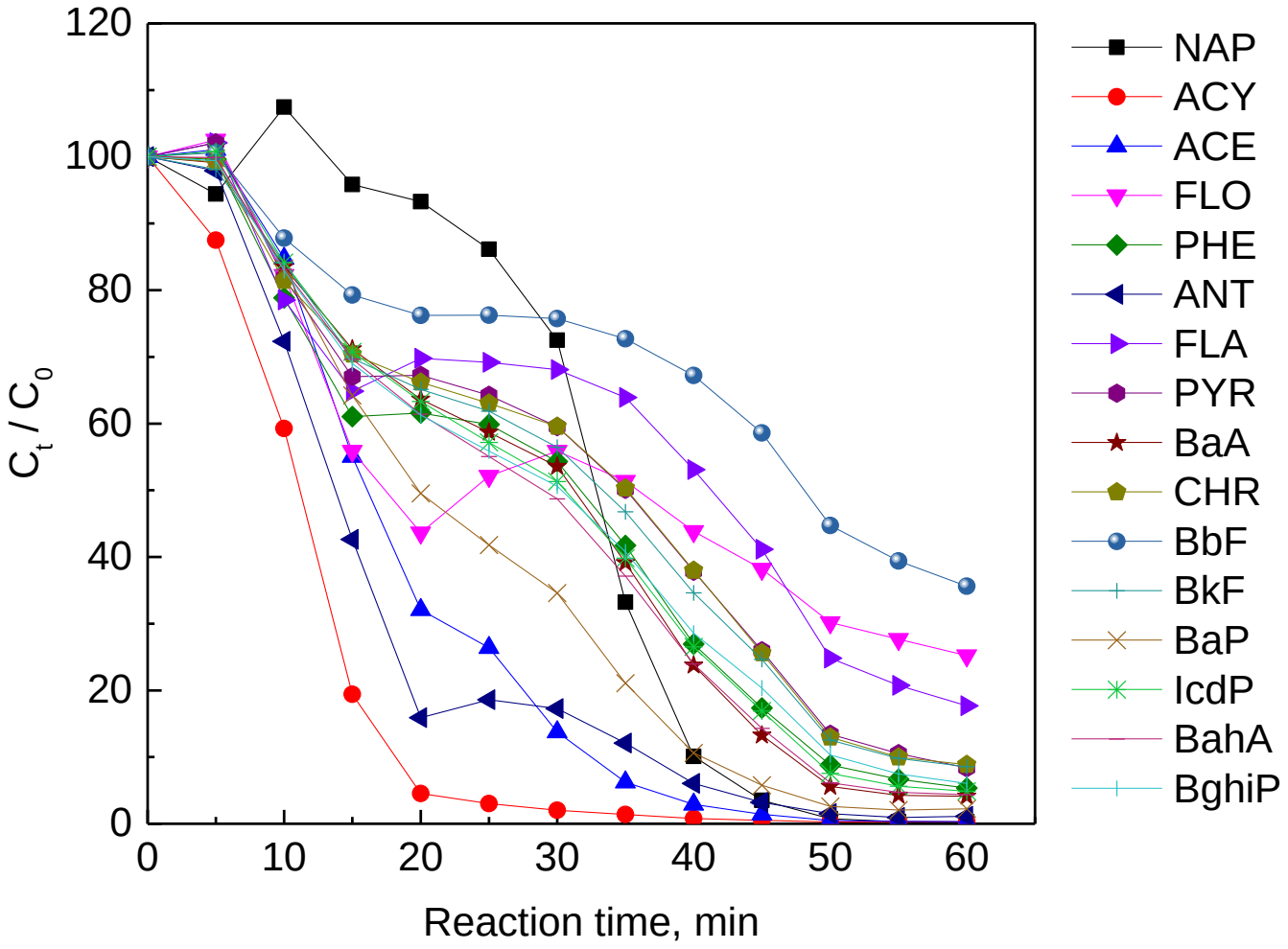


Figure 5.8 Ozonation of 16 PAHs in produced water

Overall, ozone showed strong selectivity on different 16 PAHs as the reaction constants varied significantly from 10^2 to 10^5 $M^{-1}s^{-1}$ (**Table 5.5**). This result is because the pathways tended to vary due to the structural differences. A pathway was identified for NAP by applying ozone on high concentration NAP solution (**Figure 5.9**). However, this identification was performed in deionized water solution. It is possible that the pathway can be changed in offshore produced water, for instance, the halogenation. The further oxidation may involve hydroxyl radical and oxygen which are not sufficient for cases of offshore produced water.

The major by-products of ozonation in offshore produced water were found to be trihalomethanes at a trace level (**Figure 5.10**) which means the halogenation is a major reaction of the treatment process (see **Section 5.4.3**). These by-products are carcinogenetic and may be a concern when treatment of produced water is insufficient. **Figure 5.11** shows the change of by-products concentration during ozonation. Since iodide is highly reactive to ozone, the iodine radicals were formed initially. After 15 minutes, only the triiodomethane was found in treated samples. When iodide was reacted, more ozone can be available for moderate reactive bromide. Since bromine radicals are stronger oxidative species than iodine radicals, the contaminants, intermediates, and products (including triiodomethane) were oxidized by bromine radicals to generate tribromomethane. Hydroxyl radicals slowly degraded the tribromomethane after 30 minutes. On the contrary, in the coupled UV/Ozone system, a higher level of hydroxyl radical treatment, was formed and significantly accelerated the degradation of these intermediates and end-products of ozonation. These findings were for the first time reported for produced water treatment in the literature and gave the value of integrating ozonation with UV irradiation.

Different with in a simple matrix, oil film and droplets can be formed in offshore produced water at the initial period of ozonation as shown in **Figure 5.12** and **5.13**. **Figure 5.14** demonstrates the composition of the formed oil which was highly concentrated petroleum hydrocarbons especially for longer chain aliphatic (scan mode). In comparison, there were no such phenomena observed during purging oxygen or air. The ozone or hydroxyl radicals attack the organic compounds to form organic radicals. These organic radicals can initiate the chain reaction or self-bonded, which generate larger molecules and become insoluble. As in offshore produced water, both deficiency of oxygen and a higher concentration of organic radicals can enhance this effect. There is no such effect reported in drinking water or cleaner wastewater. As a piece of evidence of synthesis effect, formed dispersed oil can absorb free dissolved PAHs (SIM mode). After the sources of polymerizable organic radicals are consumed, further oxidation of the formed oil dominates the reaction and can result in destruction and release of dissolved PAHs.

Table 5.5 Rate of constants for PAHs in ozonation process

PAHs	**Rate constant of Direct ozonation (pH < 2; t-ButOH), $M^{-1}s^{-1}$**	**Rate constant of ozonation with chain reaction (pH = 7), $M^{-1}s^{-1}$**
NAP	1500	-
ACE	108000	-
PHE	3145	10000
FLO	44.8	420
ANT	-	2700
FLA	-	950
PYR	-	3600
BaP	33200	5300
BghiP		840
CHR	10000	-

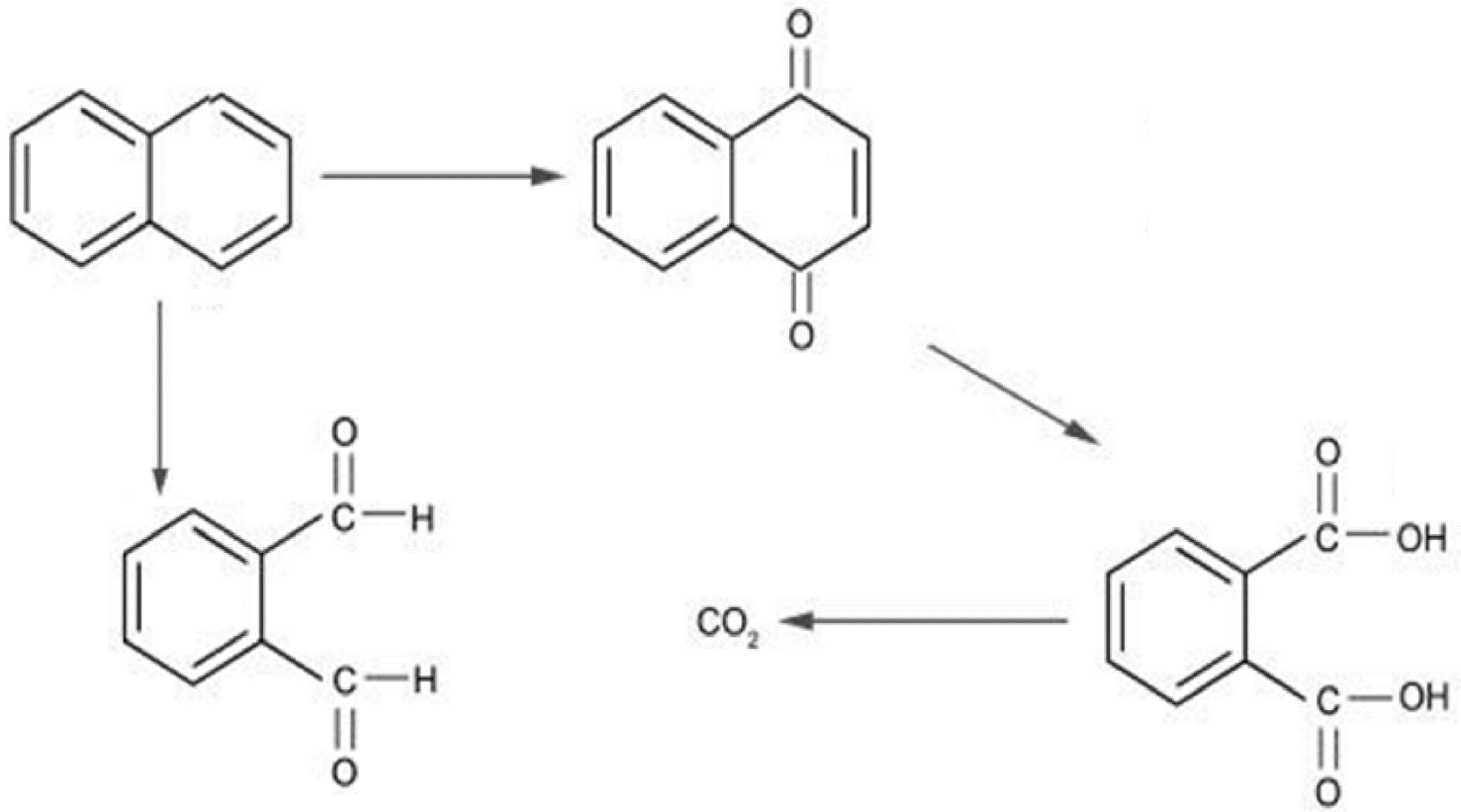


Figure 5.9 Pathway for NAP oxidation

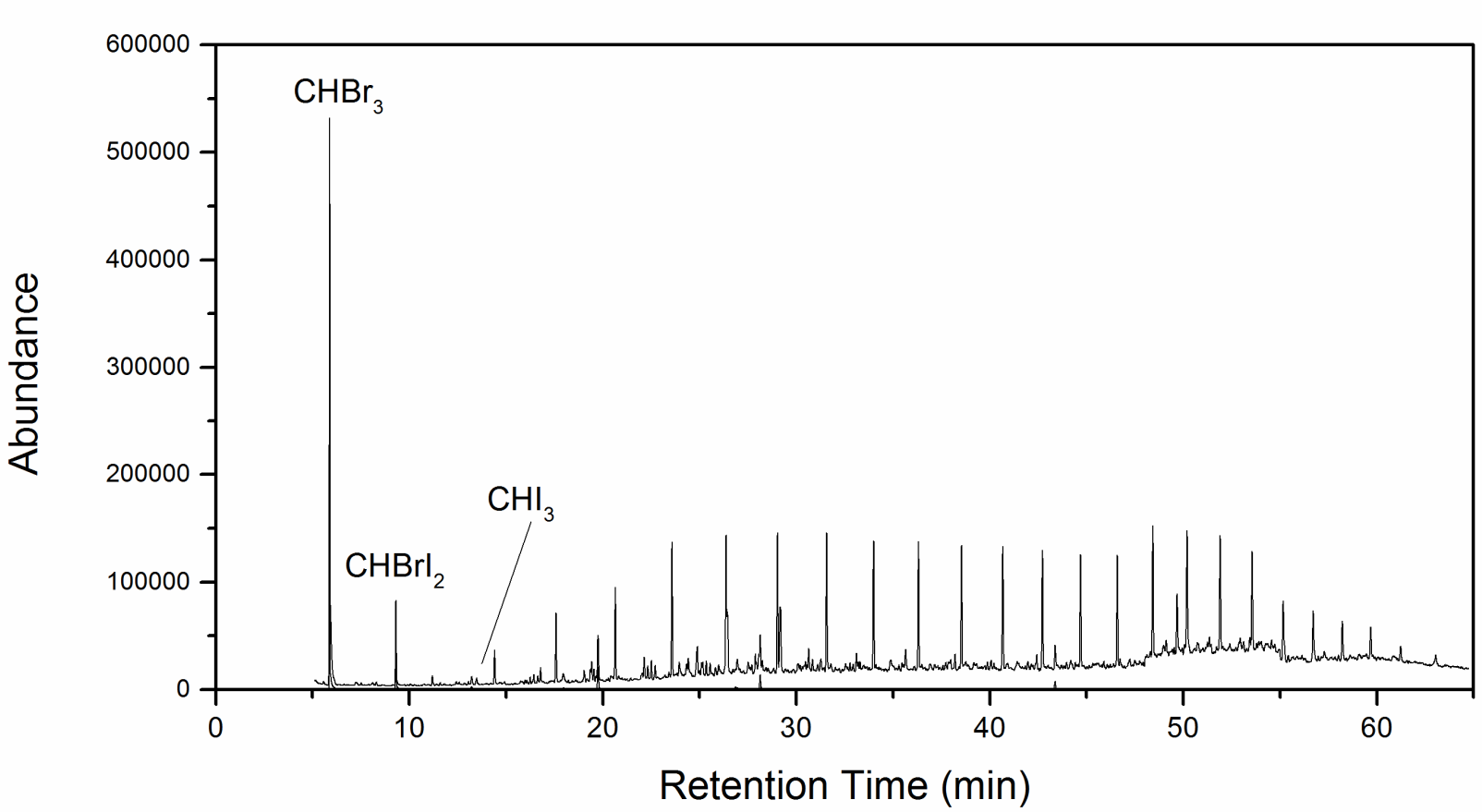
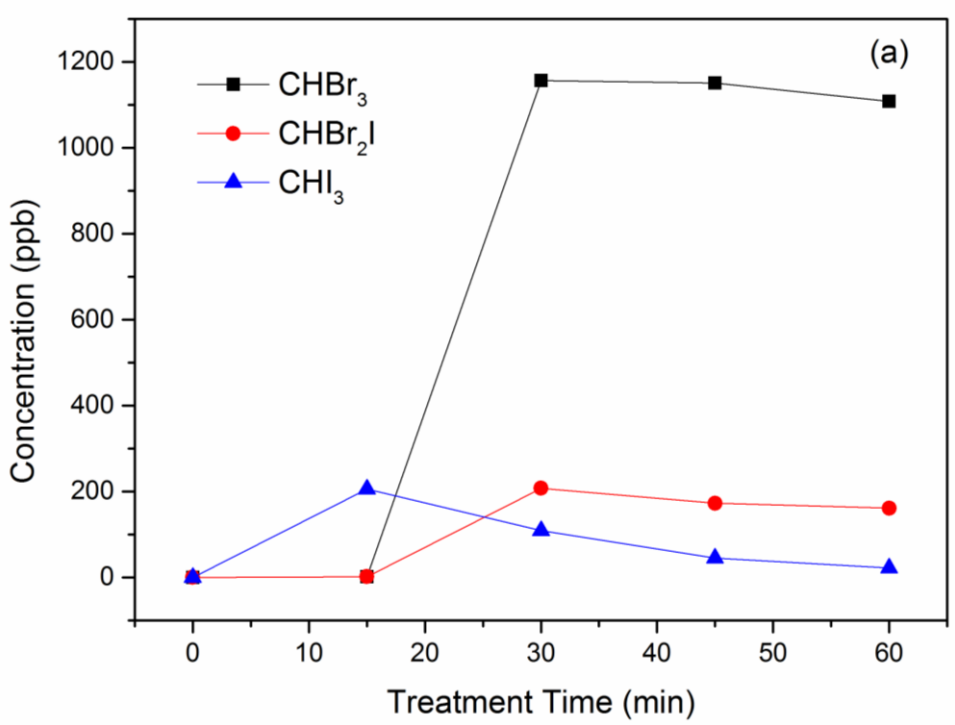


Figure 5.5 TIC chromatogram of offshore produced water after 60-min ozonation


(a)
CHBr3
CHBr2I
CHI3
Concentration (ppb)
Treatment Time (min)
0
200
400
600
800
1000
1200
0
10
20
30
40
50
60

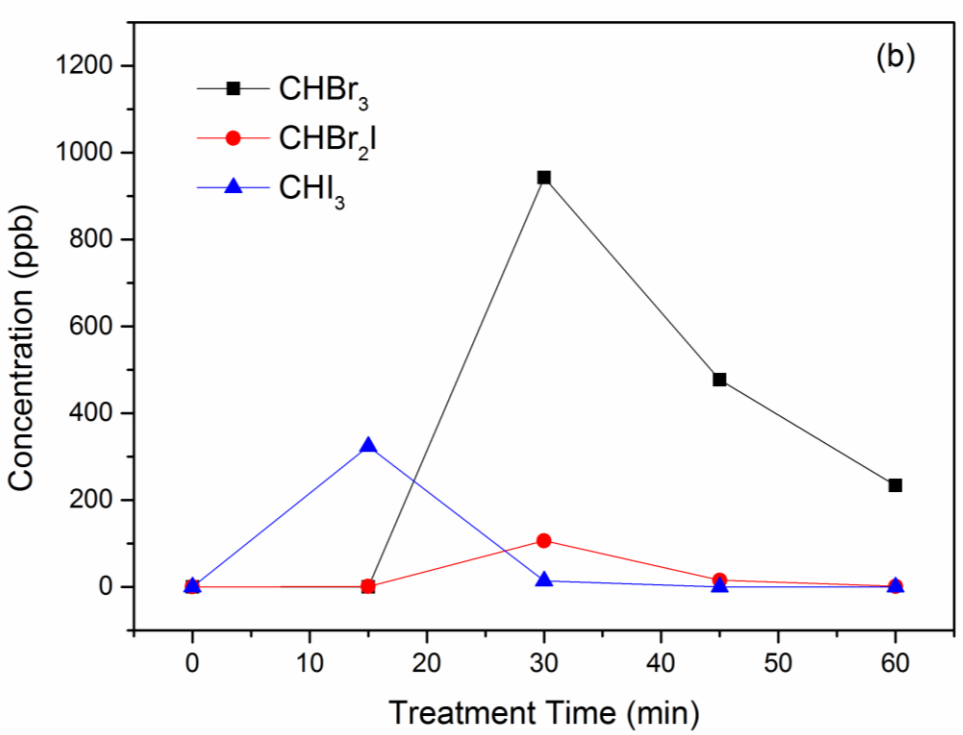


Figure 5.11 Concentration of by-products during ozonation
a) ozone; b) UV + Ozone

Since the efficient oxidation and releasing of PAHs take place simultaneously in the later period. The dissolution and oxidation lead to the non-degradation for PAHs having lower reaction constants in late time, resulting in retarded concentrations at a low level of some PAHs. This mechanism can be the biggest problem that influences the efficiency of the ozonation of produced water. It can be seen in **Figure 5.8** that, although the major trend was decreasing for all the PAHs, there were two interim increasing periods (0-5 min and 15-50 min) for some PAHs (e.g., FLO, FLA) indicating the formation and destruction of oil. For the other PAHs, lower removal efficiency was observed during these periods. Since these oil film and droplets were either at the water surface or the upper layer of water due to floatation, the sample was collected from the bottom and did not includes the PAHs in oil. So, the resulted concentration increased just for the free dissolved PAHs. The existence of these oil forms can trap the target compounds and significantly reduce the efficiency due to the involvement of mass transfer between oil and water phase. Under this condition, two decay patterns were observed for the reactions of particulate PAHs with ozone. In the first one, a total degradation was observed. In the second one, PAH degradation reached a plateau, which means that PAHs concentrations were stable regardless the increase of reaction time since the balance between the oxidation, releasing and formation.

Based on the results, three reaction schemes other than formation of PAHs by other compounds were proposed for describing the ozonation process: 1) Direct ozone reaction continuously removes the dissolved fraction of PAHs in water phase which is the major elimination pathway for PAHs removal in offshore the produced water and generates the end/byproducts such as CO_2, H_2O, and/or trihalomethanes. 2) Formation of oil and PAHs often occurs in the earlier period. The oil droplets tend to extract the dissolved PAHs and

reduce the dissolved fraction of PAHs. This process cannot eliminate PAHs since the PAHs in oil phase have limited reactivity due to the lack of water and oxidant. 3) Oxidation and destruction of oil releases the PAHs from oil (in either dissolved or dispersed form) into the free dissolved fraction (**Figure 5.15**). The rates of these three schemes tend to vary with time. The dynamic of the processes can lead to concentration increase/decrease at different stages of the ozonation process. In general, the formation of oil during ozonation can significantly inhibit the removal of PAHs in offshore produced water.

BTEX are more volatile compounds than PAHs. Rather than elimination by oxidation, they were removed mainly by the purging of ozone. Usually, for the first sampling point (5 min), all BTEX concentrations were under the detection limits for which the removal rates were larger than 90% (**Figure 5.20**).

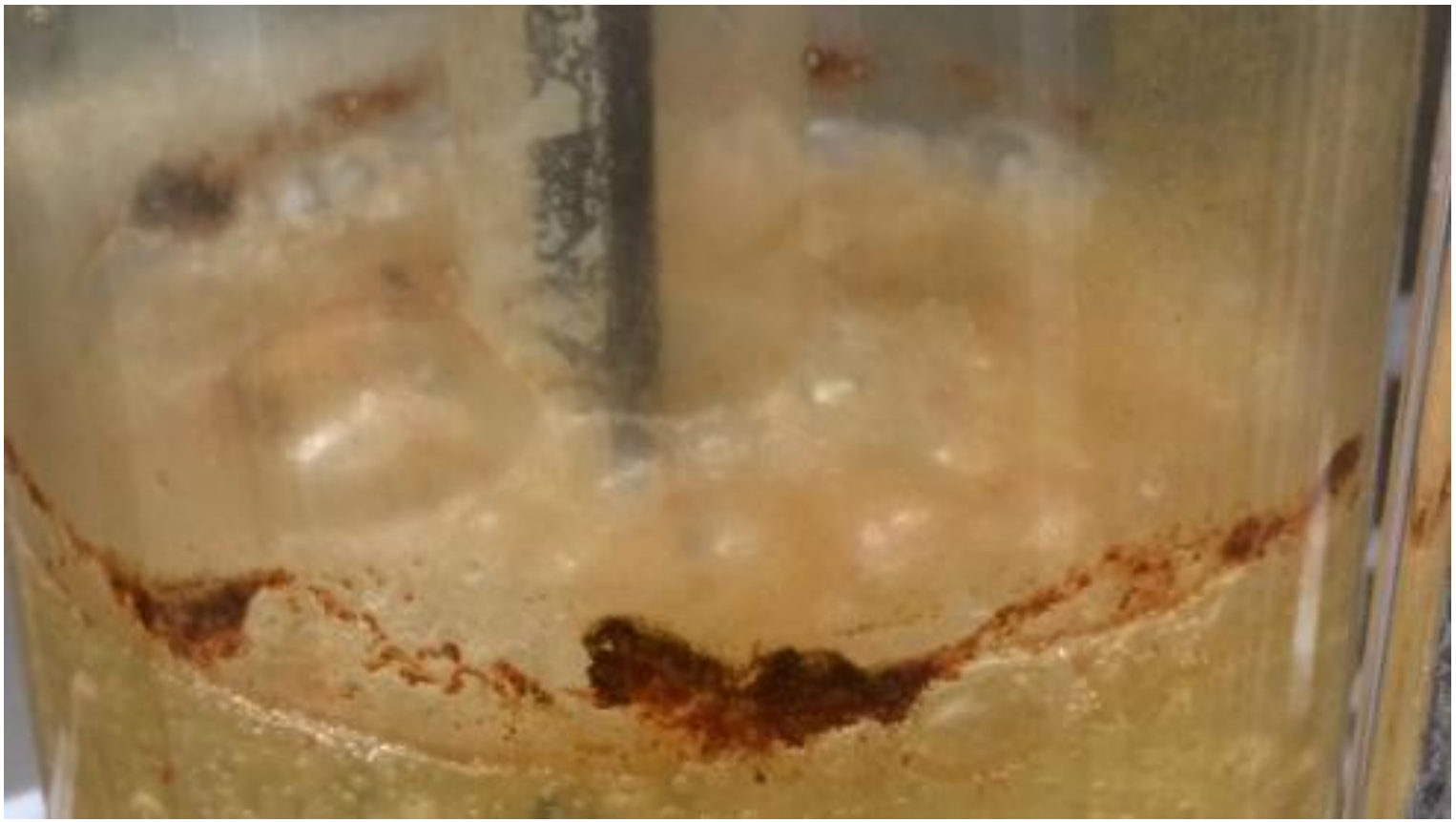
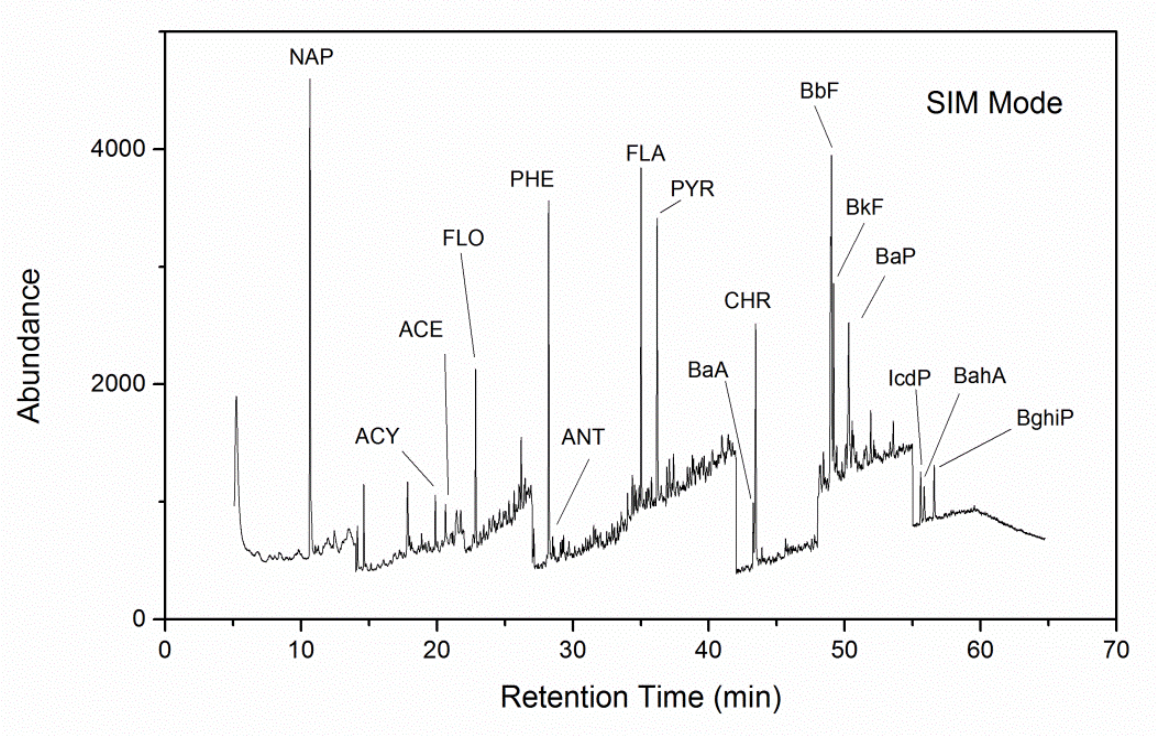


Figure 5.12 Oil film formed after 5 min of ozonation (20ppm)

Figure 5.6 Suspended oil droplets formed after 5 min of ozonation (20ppm)


NAP
ACY
ACE
FLO
PHE
ANT
FLA
PYR
BaA
CHR
BbF
BkF
BaP
IcdP
BahA
BghiP
SIM Mode
Abundance
Retention Time (min)
0
2000
4000
0
10
20
30
40
50
60
70

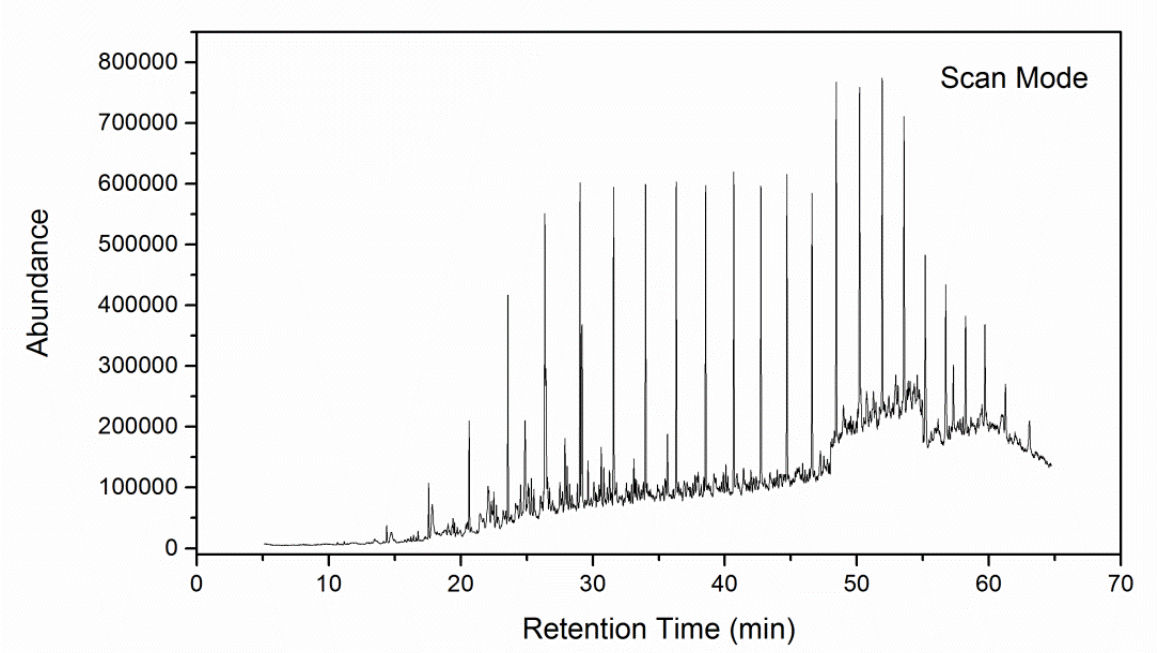


Figure 5.7 Chromatogram of formed oil during ozonation of offshore produced water

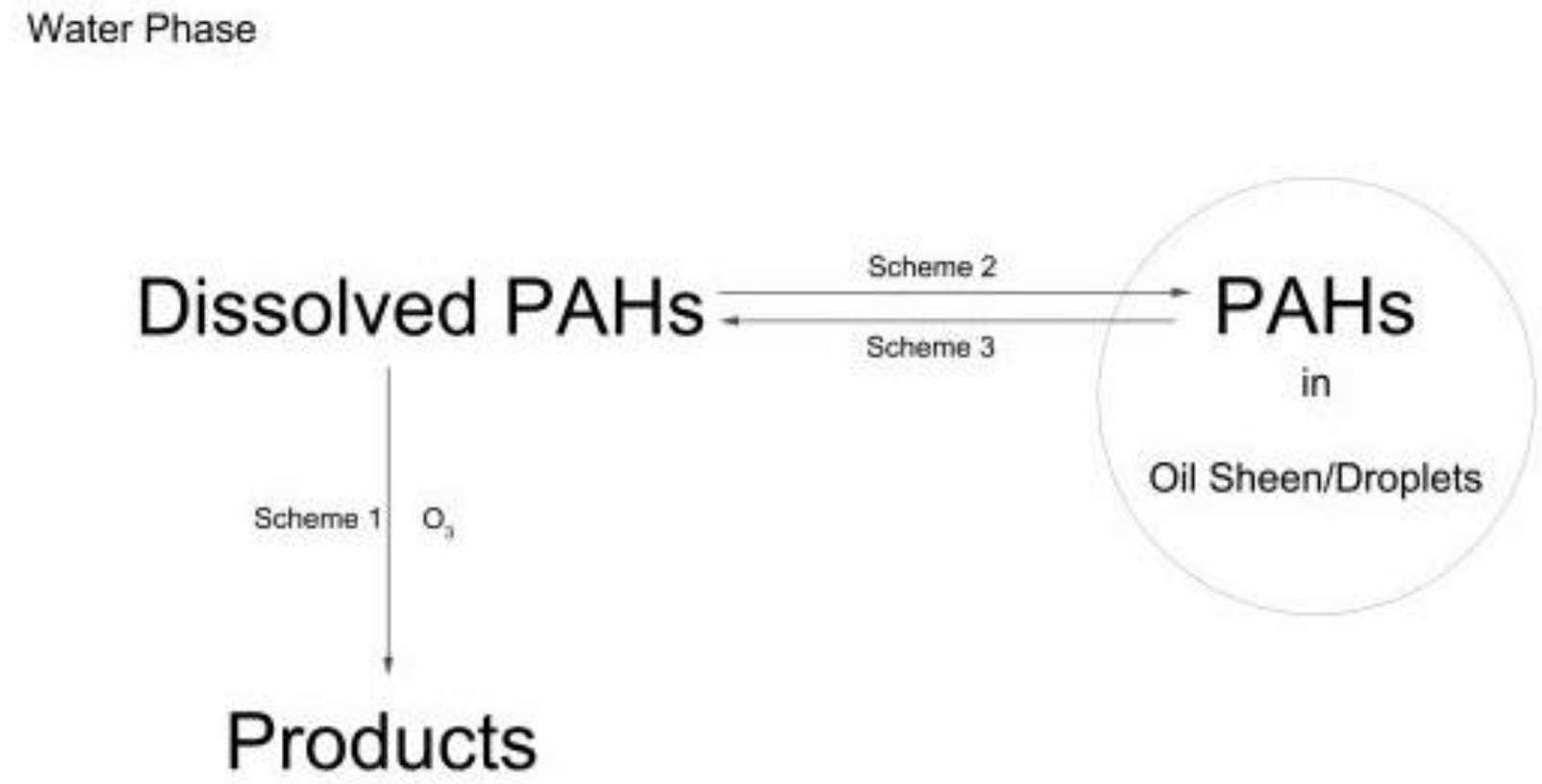


Figure 5.8 Schemes for ozonation of 16 PAHs in offshore produced water

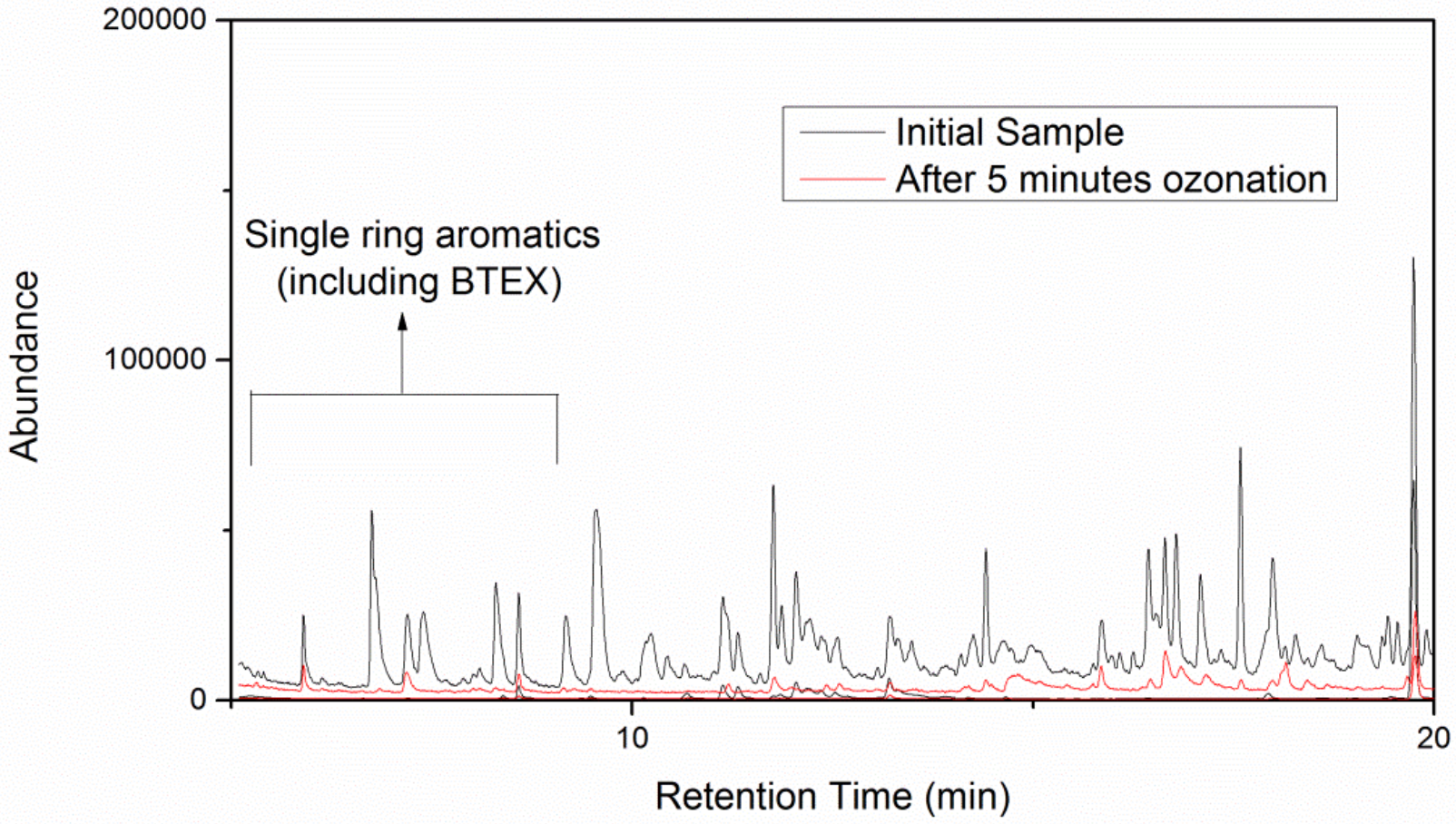


Figure 5.9 Comparison of the chromatogram of produced water before and after 5-min ozonation treatment

5.3.3 Effect of Bubble Size

The images captured regarding different bubble diffusers are shown in **Figure 5.21**. By processing these images to ImagePro®, the size of bubbles from the three different diffusers in the developed reactor are summarized in **Table 5.1**. The calibration results indicated that the different diffusers were capable of changing the bubble sizes efficiently, and a large variety of interfacial area for reaction can be consequently achieved by changing the diffusers.

A larger size of ozone bubbles on average means a smaller interfacial area for reaction, leading to a negative effect on the treatment efficiency. As shown in **Figure 5.22** (A) - (C), the decrease of bubble size could enhance the removal rate of PAHs. The lowest removal rate was 42% when the average bubble size was about 1.11 mm; average bubble size = 0.5 mm in diameter, in comparison with the rates of 60% and 80% for the average size of 0.59 mm and 0.10 mm, respectively. However, the sensitivity of removal efficiency to this factor is relative low comparing to other factors such as ozone dose and molecular structure.

5.3.4 Effect of Ozone Dose

The ozone dose can directly increase the reaction rate between ozone and chemical species including PAHs. On the other hand, the reaction between ozone and hydroxyl ions can initiate the formation of hydroxyl radicals. Therefore, a proportional relationship was observed between the ozonation efficiency and the ozone dose. As shown in **Figure 5.23**, the increase of ozone dose significantly increased the PAHs' removal rates. For the PAH species with high reaction constants such as ACY, the elimination time (removal rate greater than 95%) was reduced from to 30 minutes to 5 minutes by increasing the dose from

5 ppm to 20 ppm.

5.3.5 Effect of pH

The increase of pH can enhance the generation of hydroxyl radicals by providing more hydroxyl ion; while lower pH can raise the reaction constant by promoting the direct ozone reaction decrease the competition of ozone by the chemical species in the matrix. The change of pH affects the degradation pathway of different PAHs in offshore produced water. The results of the pH effects on the degradation of PAHs are shown in **Figure 5.24**. Comparing to the neutral pH condition, the degradation of PAHs in lower pH (acidic condition) showed better performance since the decreased competitiveness of hydroxyl ions and most PAHs prefer the direct ozone reaction rather than the degradation initiated by hydroxyl radicals. It was observed that a higher pH value (alkaline condition) led to a flower removal rates than neutral because of the increased competitiveness of hydroxyl ions to ozone and the increased hydroxyl radical concentration did not cause any significant positive effect. This result is because the hydroxyl radical has much lower selectivity, oxidation of other organic species such as alkanes could significantly compete for hydroxyl radicals with PAHs. Thus slow reaction between hydroxyl radicals and PAHs result. However, in high pH condition, the enhanced hydroxyl radical reaction accelerated the oil formation/destruction process since hydroxyl radical is a much stronger synthesis initiator and oxidizer to organic compounds.

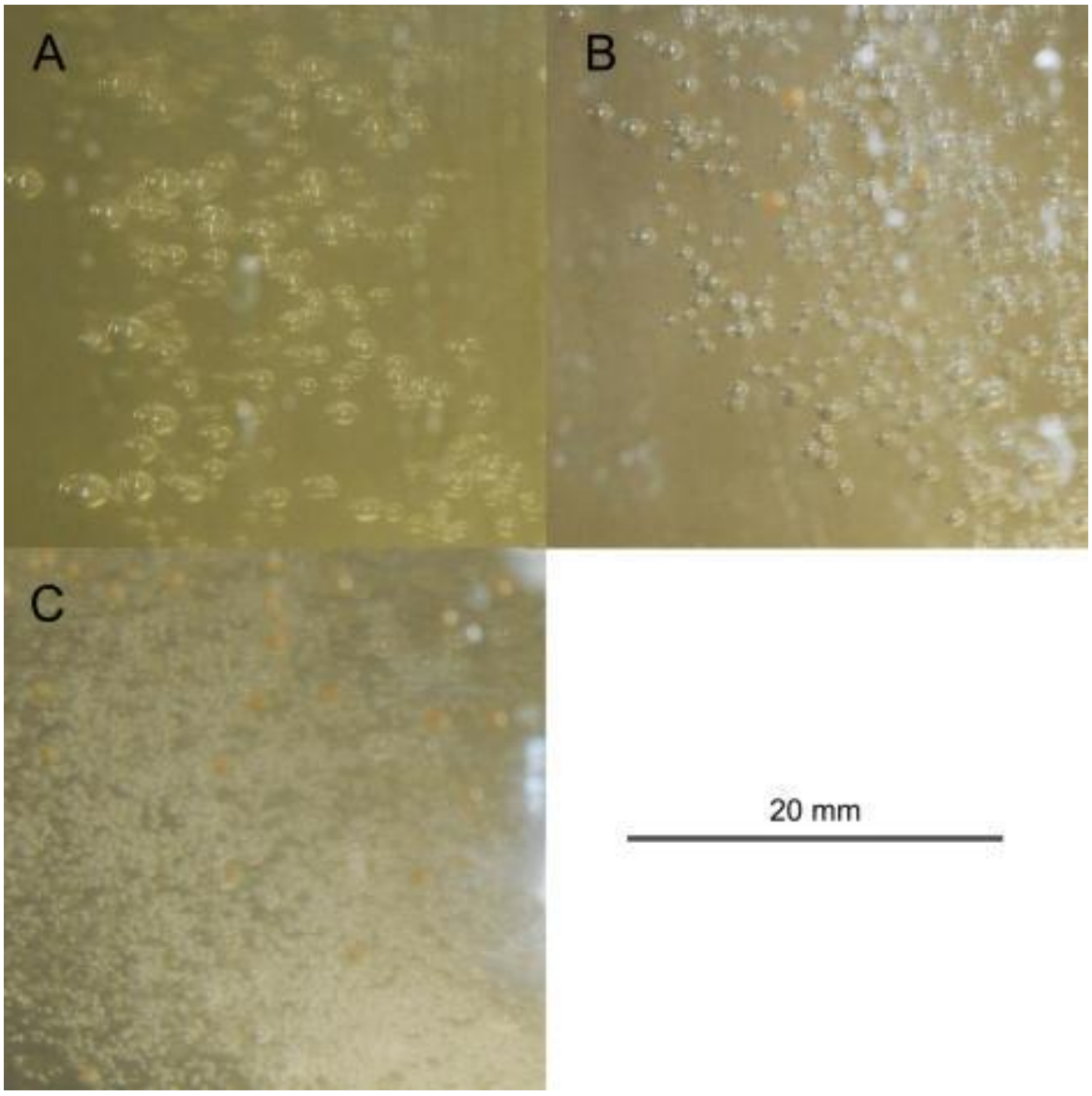


Figure 5.17 Bubbles generated by different bubble diffusers

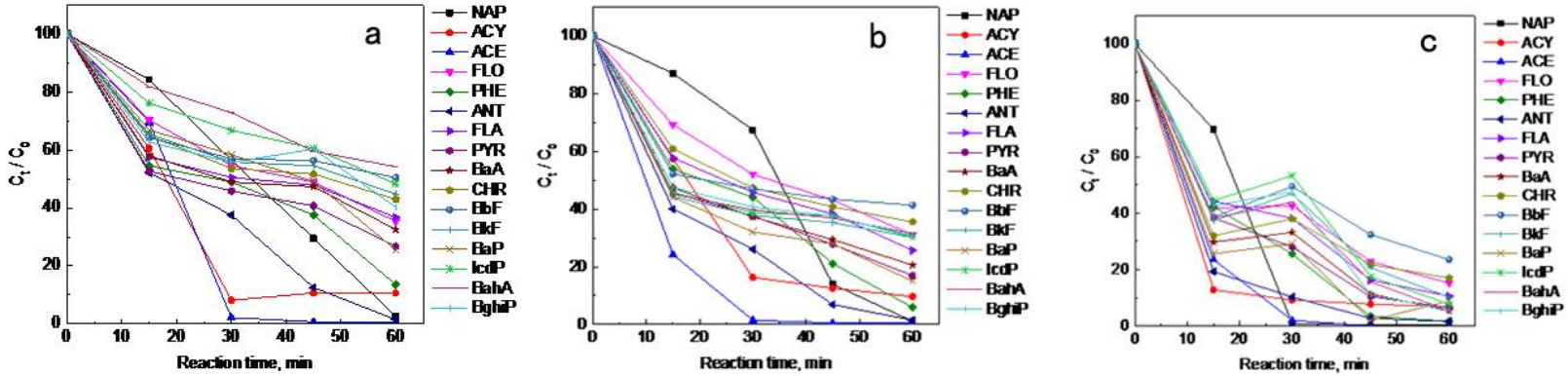


Figure 5.18 Effects of bubble size on the removal of PAHs in offshore produced water
(a) diffuser A, (b) diffuser B, and (c) diffuser C

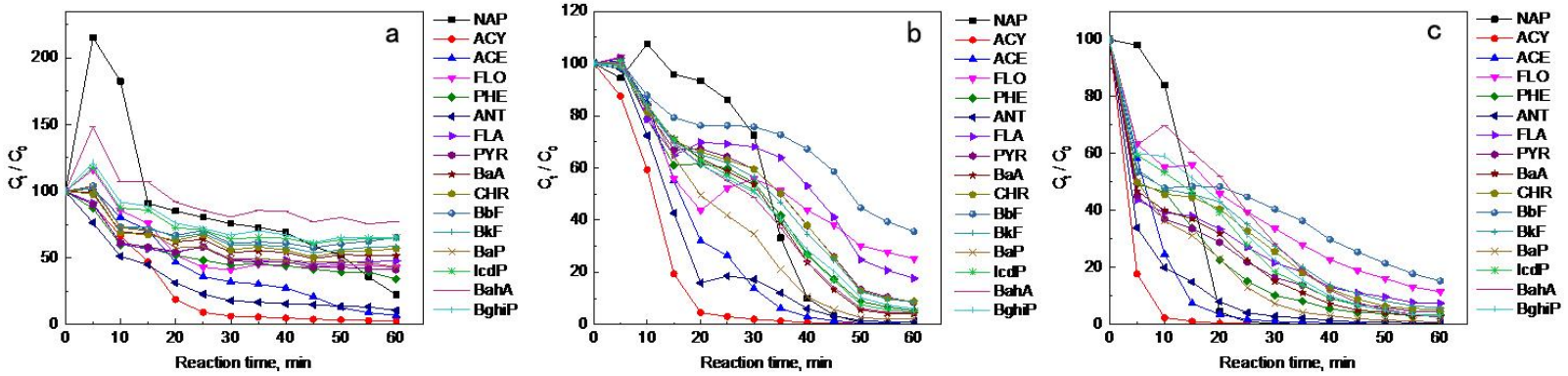


Figure 5.19 Removal of PAHs in offshore produced water with different ozone dose
(a) 5 ppm, (b) 10 ppm, (c) 20 ppm

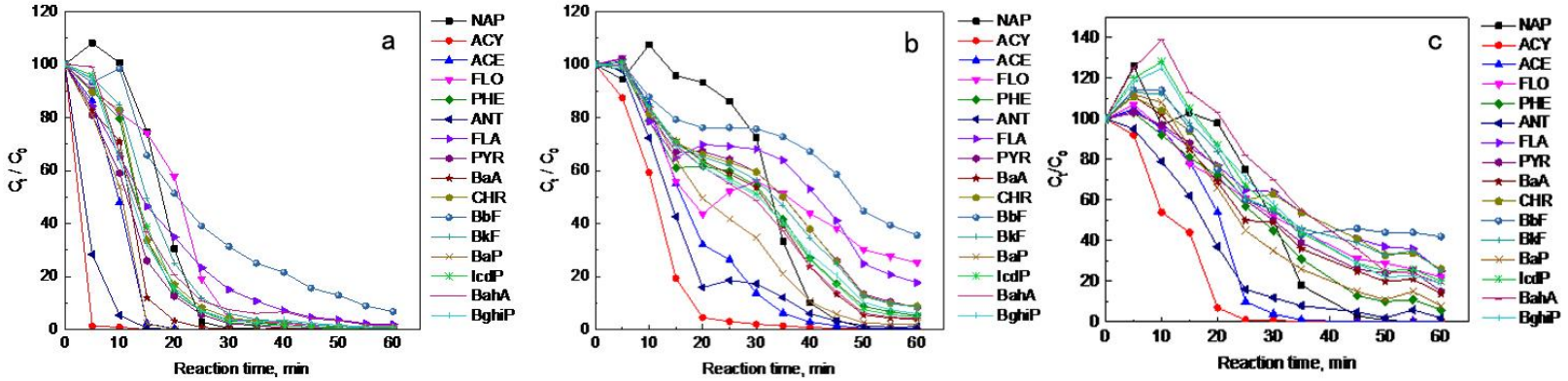


Figure 5.20 Removal of PAHs in offshore produced water at pH of (a) 3, (b) 7, and (c) 10

5.3.6 Effect of Temperature

Higher temperature can activate reactions and help the dissolution of oil drops, releasing more PAHs and other organic compounds for oxidation. Therefore, the temperature was expected to have a positive effect on the removal of 16 PAHs, which was supported by the column (1000 mL) testing results (**Figure 5.25**). When the temperature is 50 ºC, most PAHs were degraded to less than 10% of the initial concentration, while at room temperature (25 ºC) the removal rates of three PAHs were around 80% or less. The possible reason could be: 1) it might reduce the selectivity of ozone by introducing some other oxidant competitors from offshore produced water substrate; 2) it can accelerate the dissolution and change the partition of PAHs between dispersed oil and water; 3) it might enhance the destruction of dispersed oil at the final stage. The influence of temperature is more complex on offshore produced water sample than that on a simpler matrix, and the mechanisms remain unknown. Further study is required to explain this effect.

5.3.7 UV Enhanced Ozonation

The ozonation can be enhanced by UV irradiation since more hydroxyl radicals can be generated from ozone irradiated by UV. **Figure 5.26** shows the removal efficiency of 16 PAHs by ozone alone and UV/ozone. The results indicate that the enhancement by UV was not significant in the beginning (before 15 min) but increases at the later stage (after 15 min). The possible reason is that at the initial period, the ozone at the interface or aqueous phase immediately reacted with the chemical species such as I^-, Br^- and Fe^{2+}. Therefore, less dissolved ozone could exist in the aqueous phase to generate the hydroxyl radicals. On the other hand, due to the competitiveness of produced water substrate, the hydroxyl

radicals cannot enhance the reduction. Since the UV might consume a fraction of ozone, it could also slightly reduce the efficiency. At a later period, the competition by the other organic species was reduced, then the enhancement was observed. For example, the removal rates for FLO and BbF were increased from 86% to 91% and from 84% to 91% respectively. BaA, CHR, and BbF were all resistant in ozonation, but integration with UV irradiation enhanced the degradation.

Although only slightly enhancement of PAHs degradation by UV-enhanced ozonation compared with ozonation alone in the same condition, the effect of UV on the reduction of ozonated by-products (iodoform, bromoform, etc.) was significant. As in **Figure 5.11**, the concentration of these by-products was controlled by the 60-min UV-enhanced treatment. When the UV irradiation was applied, the generation of idioform was higher at the first 15 minute and followed by a rapid decrease of all other by-products, such as bromoform was found after 30 min treatment. It indicates that the generation of hydroxyl radicals by UV irradiation can accelerate not only the production of by-products but also the degradation of these intermediates and end-products.

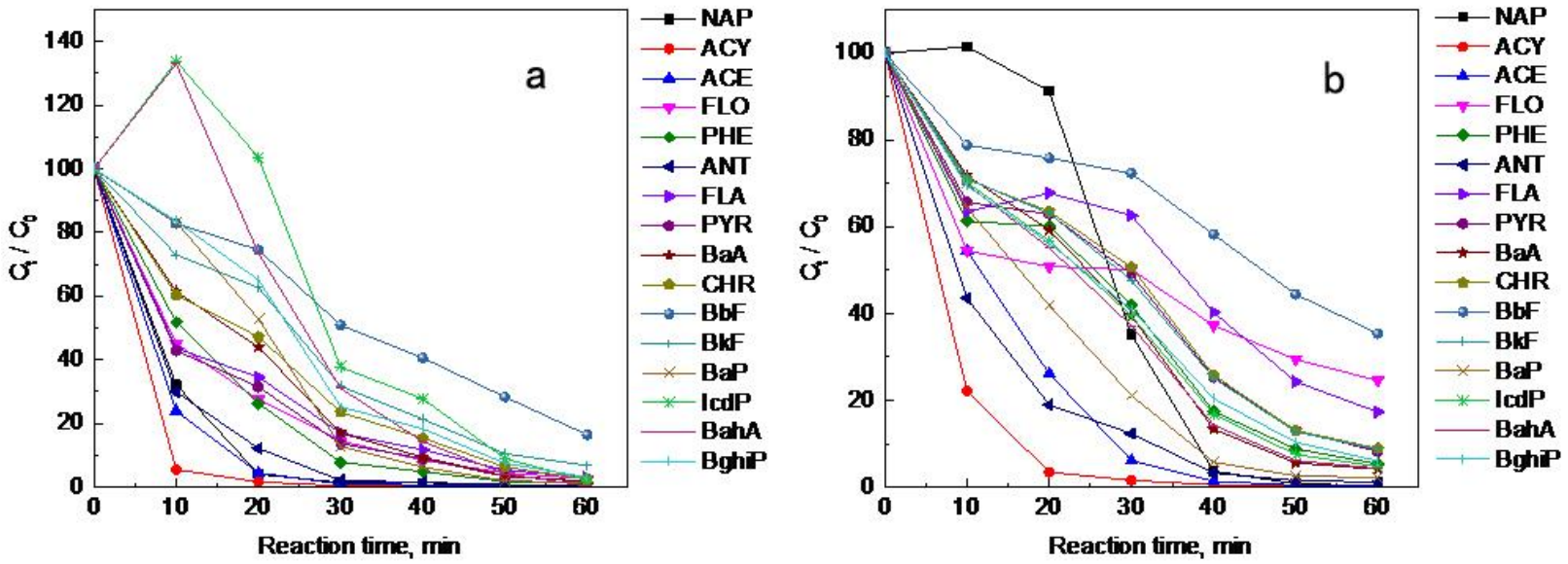


Figure 5.21 Effect of temperature on removal of PAHs in offshore produced water by a column test at (a) 25 and (b) 50 °C

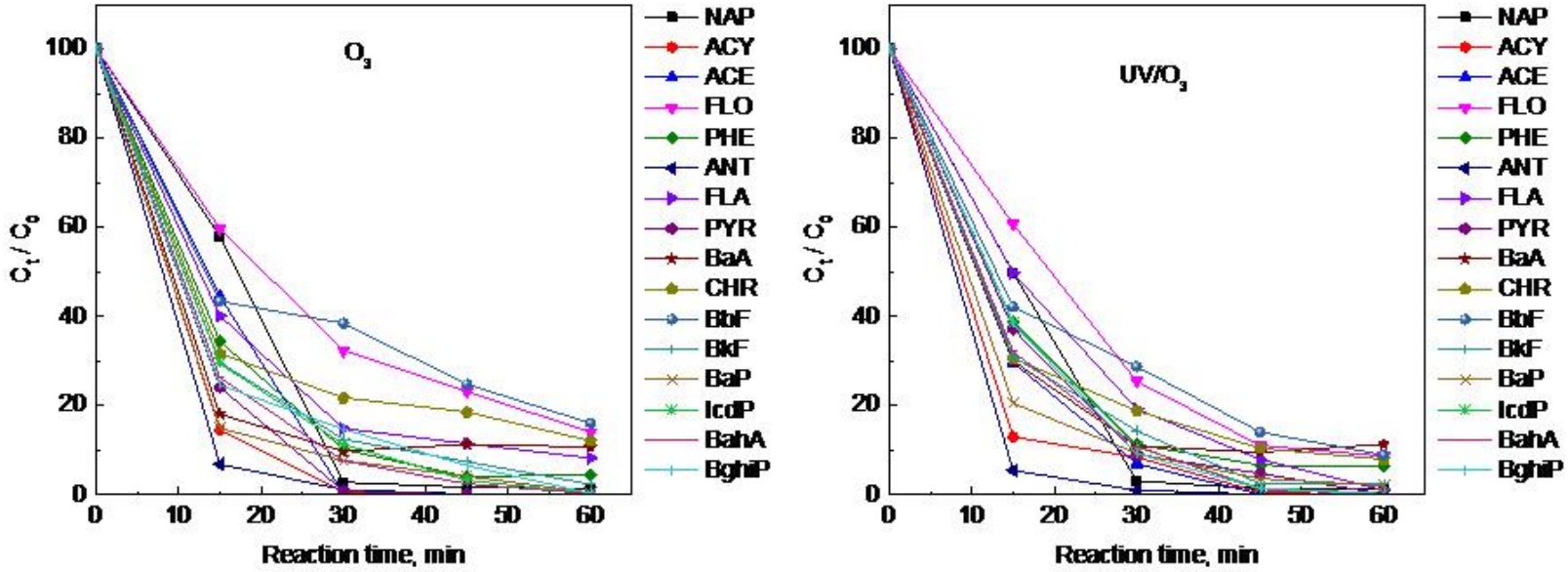


Figure 5.22 Oxidation of PAHs in produced water by ozonation and UV/Ozone

It was observed that the oil formation/destruction process was accelerated during UV-enhanced ozonation and the DOC concentration of produced water was increased from 103 mg/L to 130 mg/L after treatment. It was reported that the halogenated organics have higher resistance to oxidative reagents such as dichromate and oxygen (high-temperature). The hydroxyl radical thus may play a major role since hydroxyl radical is much more reactive to the halogenated hydrocarbons to produce phenols alcohols and acids. Further research is needed to identify the key roles of formed oil in the degradation of PAHs in these treatment methods.

5.3.8 Kinetics and Modeling Ozonolysis

When two reactions simultaneously exist in a water sample, the following equations can describe the consumption of ozone:

$$M + O_3 \rightarrow P$$

$$\frac{d[O_3]_M}{dt} = k_M [O_3][M] \qquad (1)$$

$$A + O_3 \rightarrow P$$

$$\frac{d[O_3]_A}{dt} = k_A [O_3][M] \qquad (2)$$

where M and A are the substances in water, P is the product, $[O_3]$ is the ozone concentration in a bubble and the $d[O_3]_M$ and $d[O_3]_A$ are the ozone deficiency caused by M and A respectively. k_M and k_A are the reaction constants. So, the total ozone deficiency can be the sum of the previous reaction which can be described as follows:

$$\frac{d[O_3]}{dt} = \frac{d[O_3]_M}{dt} + \frac{d[O_3]_A}{dt} = k_M[O_3][M] + k_A[O_3][M] = [O_3]\left(k_M[M] + k_A[M]\right) \quad (3)$$

Thus, the ozone deficiency caused by A can be calculated by Equation 4

$$\frac{d[O_3]_A}{dt} = \frac{k_A[M]}{k_M[M] + k_A[M]}\left(k_M[M] + k_A[M]\right)[O_3] = \frac{k_A[M]}{k_M[M] + k_A[M]}\frac{d[O_3]}{dt} \quad (4)$$

Based on this theory, the ozone deficiency resulting from single species can be expressed as

$$\frac{d[O_3]_{PAH}}{dt} = \frac{k_{PAH}[PAH]}{\sum k_i[i]}\frac{d[O_3]}{dt} \quad (5)$$

Where i is the chemical species in offshore produced water. Since the aqueous concentration of ozone is maintained at 0 at the initial period, mass transfer between the gas phase and aqueous phase can be treat as a component (I) and be expressed in the form of

$$\frac{d[O_3]}{dt} = k_L a[O_3]_L^* = k_L a H_e[O_3] = \frac{k_L a H_e}{\sum k_i[i]}\frac{d[O_3]}{dt} \quad (6)$$

Where $[O_3]_L^*$ is the saturated aqueous ozone concentration, k_L is the diffusion constant, a is the interfacial area, and H_e is Henry's law constant.

For a single ozone bubble, when it is transmitting in the water, the ozone in the bubble can be continually absorbed with the water sample. By assuming the ability of absorbance or reactivity of the water sample is k_{LM} [M], the ozone deficiency caused by water sample can be expressed as,

$$\frac{d[O_3]}{dt} = k_{LM} a[O_3][M] \quad (7)$$

Where $[O_3]$ is the concentration of ozone in the gas phase. As the retention time of ozone bubble in the sample is t_r, by integration of Equation 7, the following relationship between ozone concentration at inlet and outlet can be obtained

$$\frac{[O_3]_{outlet}}{[O_3]_{inlet}} = e^{-k_{LM} a [M] t_r} \qquad (8)$$

moreover, t_r can be expressed as

$$t_r = \frac{b}{u} \qquad (9)$$

Where b is the column height and u is the velocity of the bubble at treatment time t. So, the reacted ozone in single ozone bubble can be calculated by

$$\frac{d[O_3]^t_{bubble}}{dt} = [O_3]\left(1 - e^{-k_{LM} a [M] \frac{b}{u}}\right) \qquad (10)$$

Where $[O_3]$ here and in all following Equations is defined as the **ozone concentration in the inlet gas** and the total ozone deficiency of ozone mass at time t can be calculated by

$$\frac{d[O_3]}{dt} = Q[O_3]\left(1 - e^{-k_{LM} a [M] \frac{b}{u}}\right) \qquad (11)$$

The relationship between the ozone deficiency caused by PAHs and the oxidized PAHs can be described by using stoichiometric factor Z_{PAH} By combination of the competition kinetics with the ozone deficiency kinetics; the following equation can calculate reaction rate of PAHs

$$\frac{d[PAH]}{dt} = \frac{dM_{PAH}}{V_L dt} = \frac{Z_{PAH}}{V_L}\frac{dM_{O_3}}{dt} = \frac{Z_{PAH}}{V_L}\frac{k_{PAH}[PAH]}{\sum k_i [i]}[O_3]\left(1 - e^{-k_{LM} a [M] \frac{b}{u}}\right) \qquad (12)$$

However, this equation cannot be integrated, and finite method must be introduced.

Thus, the removal efficiency can be expressed as Equation 7-13 by applying the time fragments as 1 second

$$\frac{[PAH]_t}{[PAH]_0} = \prod_0^t e^{\frac{Z_{PAH} k_{PAH}}{V_L k_{LM} a[M]}[O_3]} \left(1 - e^{-k_{LM} a[M]\frac{b}{u}}\right) \qquad (13)$$

By solving Equation 13, a simulation can be obtained for individual PAH (**Figure 5.27**). ACE was selected as probe compound since it has a high degradation rate and its trend is clearer due to the interference by produced water substrate is smaller. The results show that the modeling has good prediction with the process. The difference of the data at 10 and 25 minutes can be majorly contributed from the formation and destruction of the oil film and droplets. The good correlation indicated that the significance of competitiveness between target PAHs and the produced water substrate.

The operational parameters were examined to examine the kinetics.

Ozone concentration

In practice, the ozone concentration can change the dynamic of the sample matrix reactivity significantly. However, the relationship between ozone dose and the matrix reactivity has not been identified. Therefore, the uniform dynamic was assumed. From **Figure 5.28**, the ozone concentration has a significant positive effect on the removal efficiency, which is correlated with the experimental results.

Reactivity of PAHs

The reactivity of PAHs also showed a significant effect on the efficiency. Its effect on the final removal efficiency has been demonstrated in **Figure 5.29**, which showed that the

higher removal rate could be achieved by higher reaction constant. This model indicated that the removal rates are very sensitive to selectivity, as such, a significant variability exists between different PAHs in the experimental results.

Interfacial Area

The variation of bubble size can lead to the change of interfacial area. The interfacial area is inversely proportional to the bubble size. However, the results (**Figure 5.30**) showed that the bubble size had a relatively small effect on the removal efficiency in the range of 0.01 mm to 0.1 mm, which is correlated with the experiment result that the bubble size has a smaller effect than other factors.

5.4 Mechanistic Analysis of Substrate Impact

5.4.1 Dynamic Oxidant Competitiveness

Oxidants initiate the transformation of both target compounds (PAHs) and the other reactive species in the produced water substrate. In the case of UV photolysis, the photon can be absorbed by species such as I^-, phenols, and other compounds have a significant light absorbance in the emission range (wavelength) of UV other than PAHs. The light-induced reaction usually has high selectivity regarding the wavelength. Therefore, there is a significant variability in degradation rates between species. Since produced water contains abundant different kinds of compounds, the are species can compete for the light with PAHs and react with it, resulting in that the target pollutants can absorb only a fraction

of light. This mechanism is one of the major reasons that the produced water substrate pose inhibition effect on the removal of target pollutants. Virtually, the higher reactivity (distinction coefficient) the compound has, the higher competitiveness it has. Meanwhile, the higher the concentration of the species is, the higher the competitiveness they have. So, the competitiveness of a compound in such system is related to its concentration and reactivity. However, after absorption of light, the compound can be transformed into other species which may have lower or higher reactivity with the oxidant leading to a change of competitiveness. Therefore, the competitiveness of species is changing along with the treatment time. In the case of photolysis, the attenuation coefficient which is competitiveness of produced water substrate is changing along with treatment time, which is shown in **Section 4.3**. Since the initial concentration of PAHs is relative low, the PAHs thus sensitive to the competitiveness of other species, resulting in the changed degradation trends of PAHs rather than the first-order reaction. Therefore, the kinetic model developed in this research involving dynamic competitiveness performed better prediction.

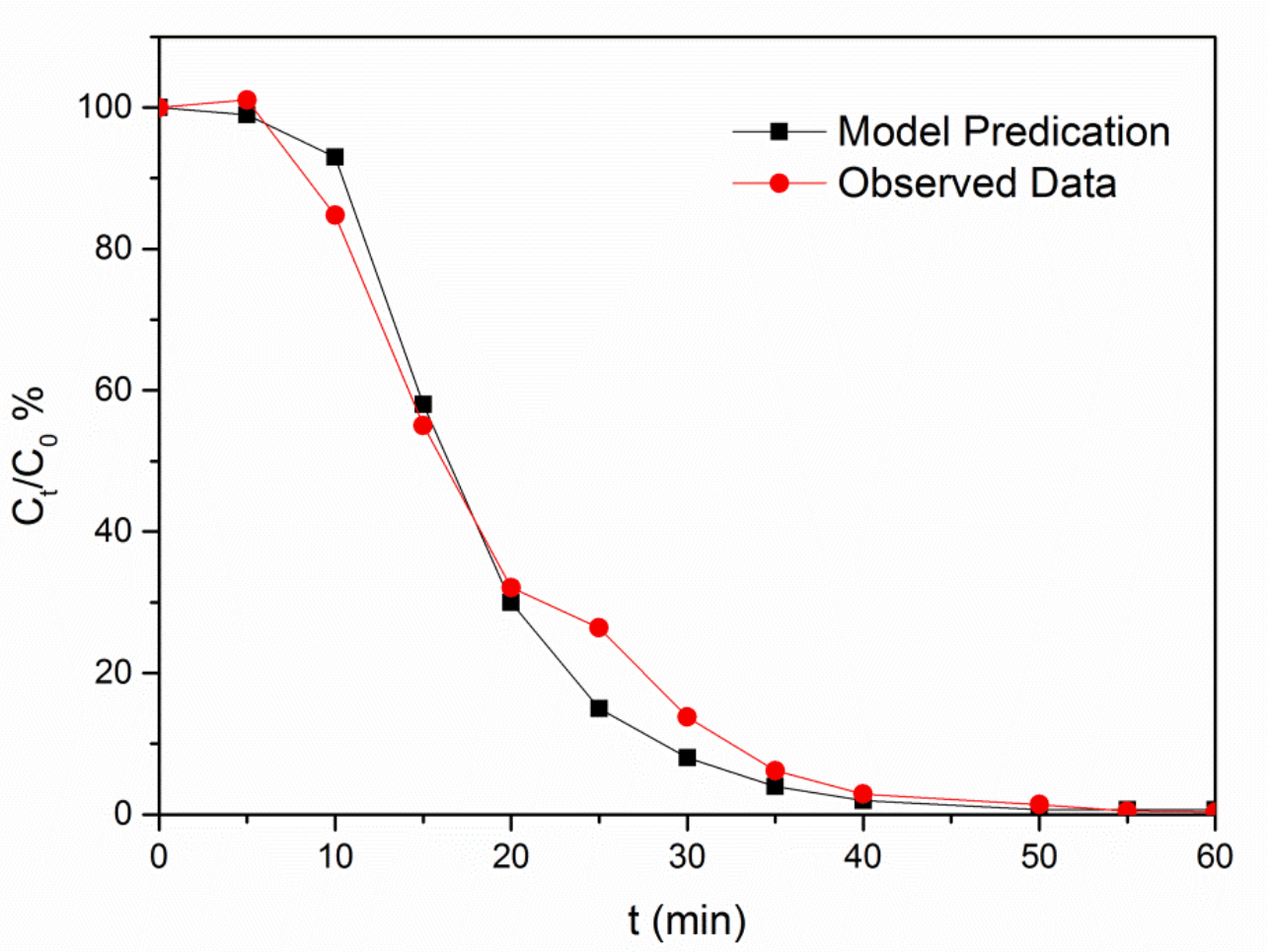


Figure 5.10 Modeling of ACE oxidation in produced water by direct ozone reaction

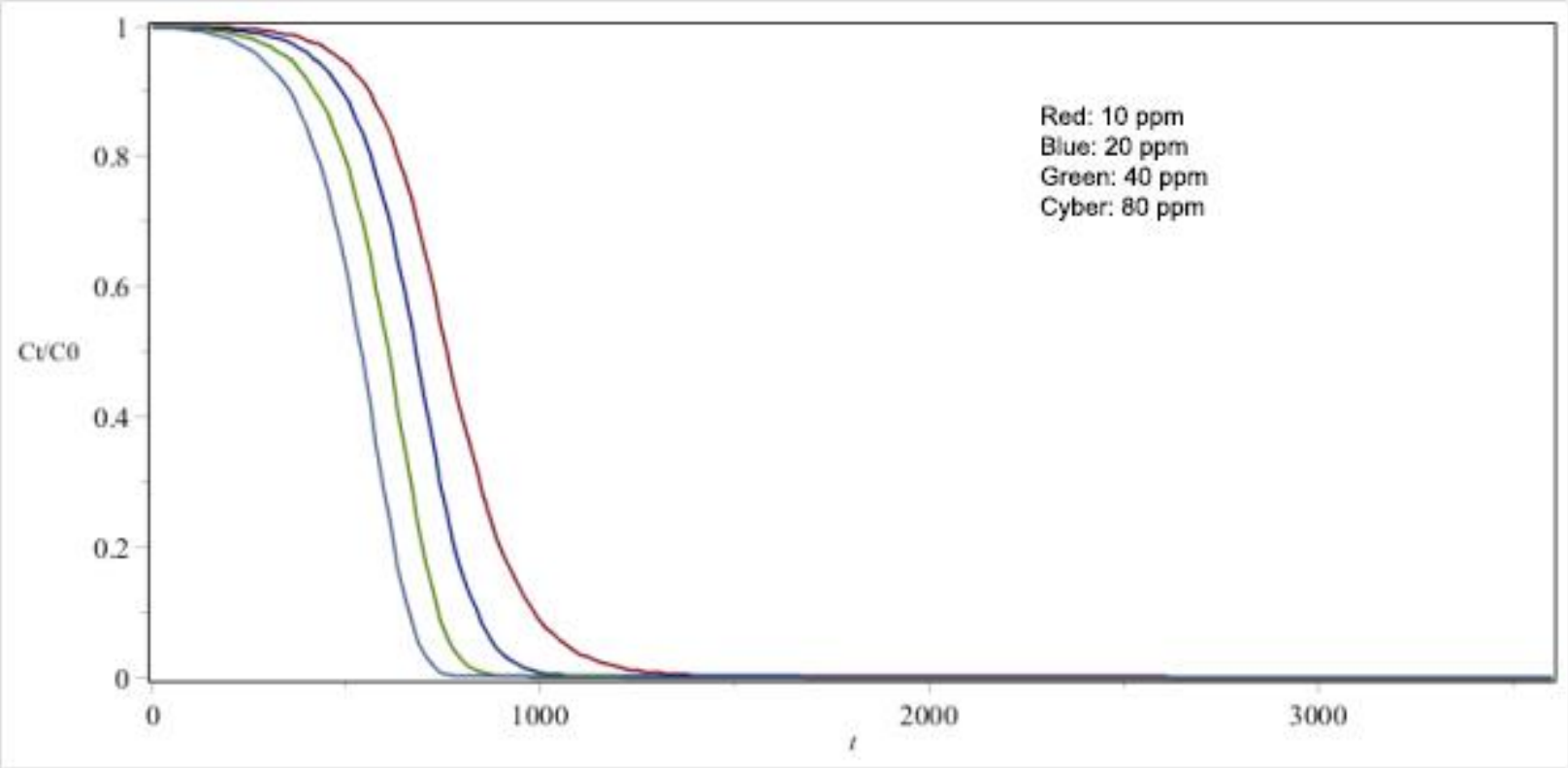


Figure 5.11 Predicted effect of ozone inlet gas concentration

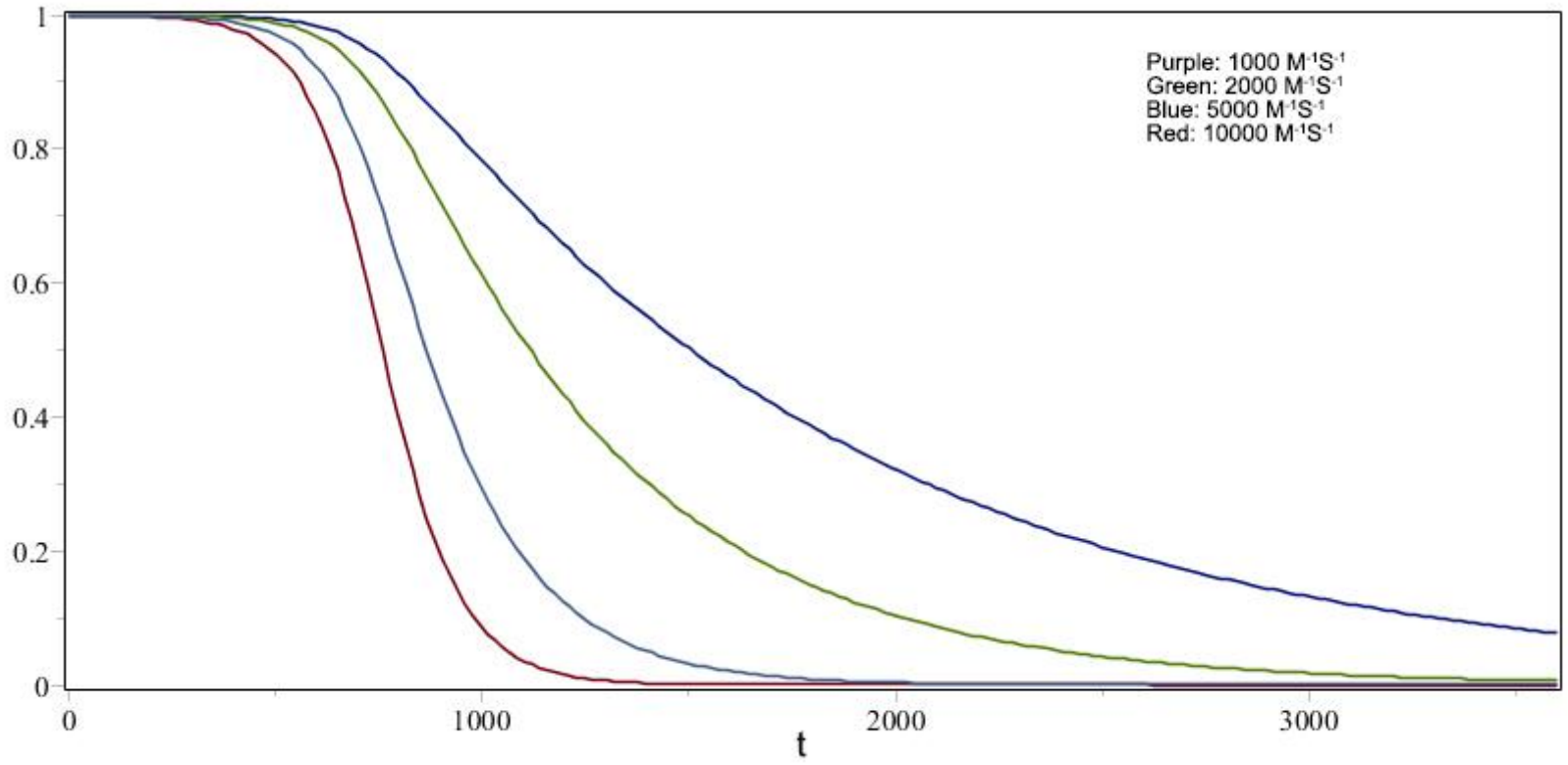


Figure 5.12 Predicted effect of the PAHs reactivity

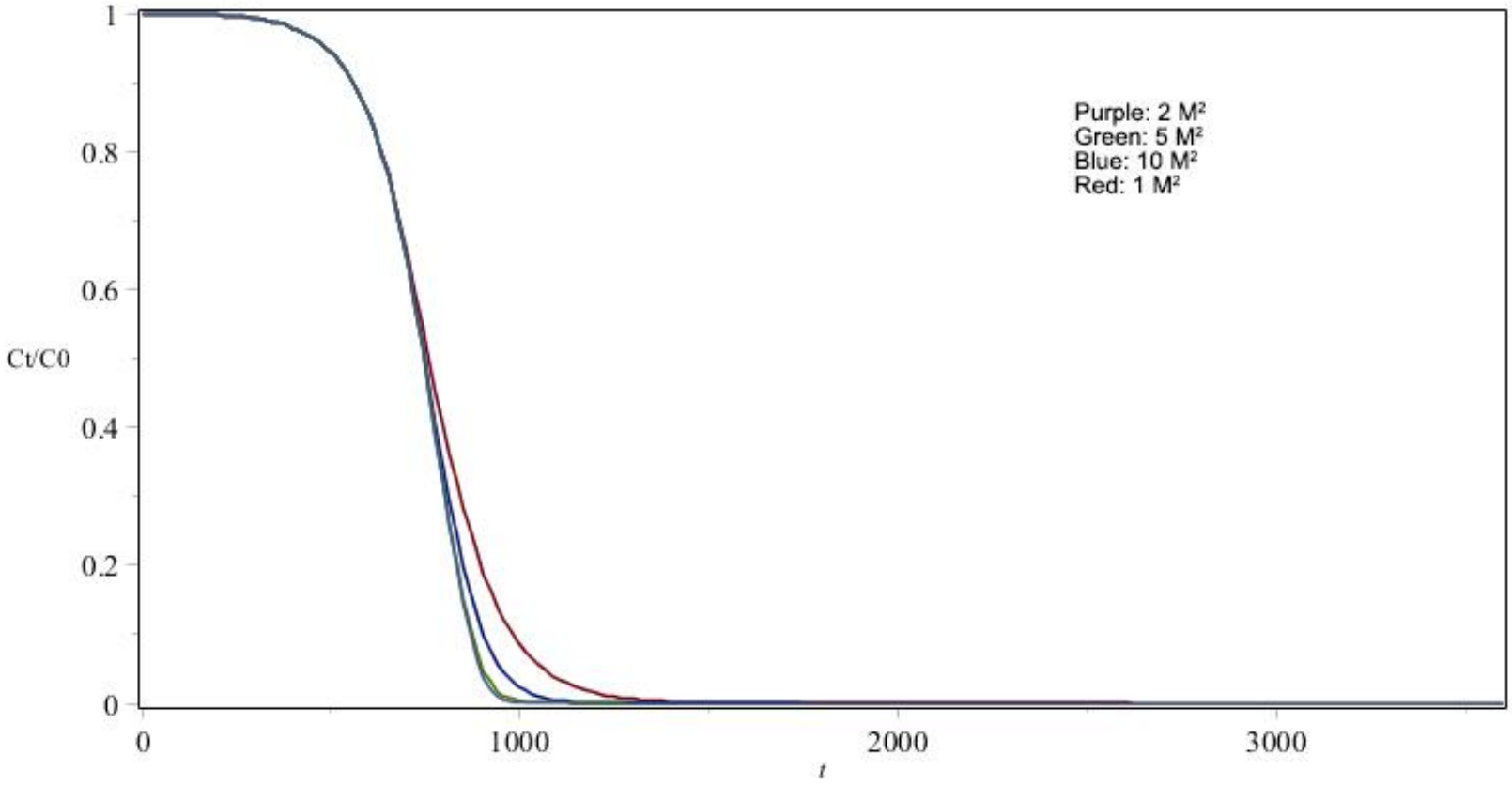


Figure 5.13 Predicted effect of interfacial area

Table 5.6 Referred Microtox EC_{50} values for the individual components in produced water
(Wells *et al.*, 1997)

Compound	Microtox EC_{50} 5min, mg/L
phenol	15.1
NAP	0.90
ANY	0.34
ANA	0.75
PHE	0.48
FLO	0.50
ANT	0.64
BaA	0.73
FLA	0.83
CHR	0.92
BaP	10.7
PYR	>500
PHE+CHR+ANT+BaP	0.6

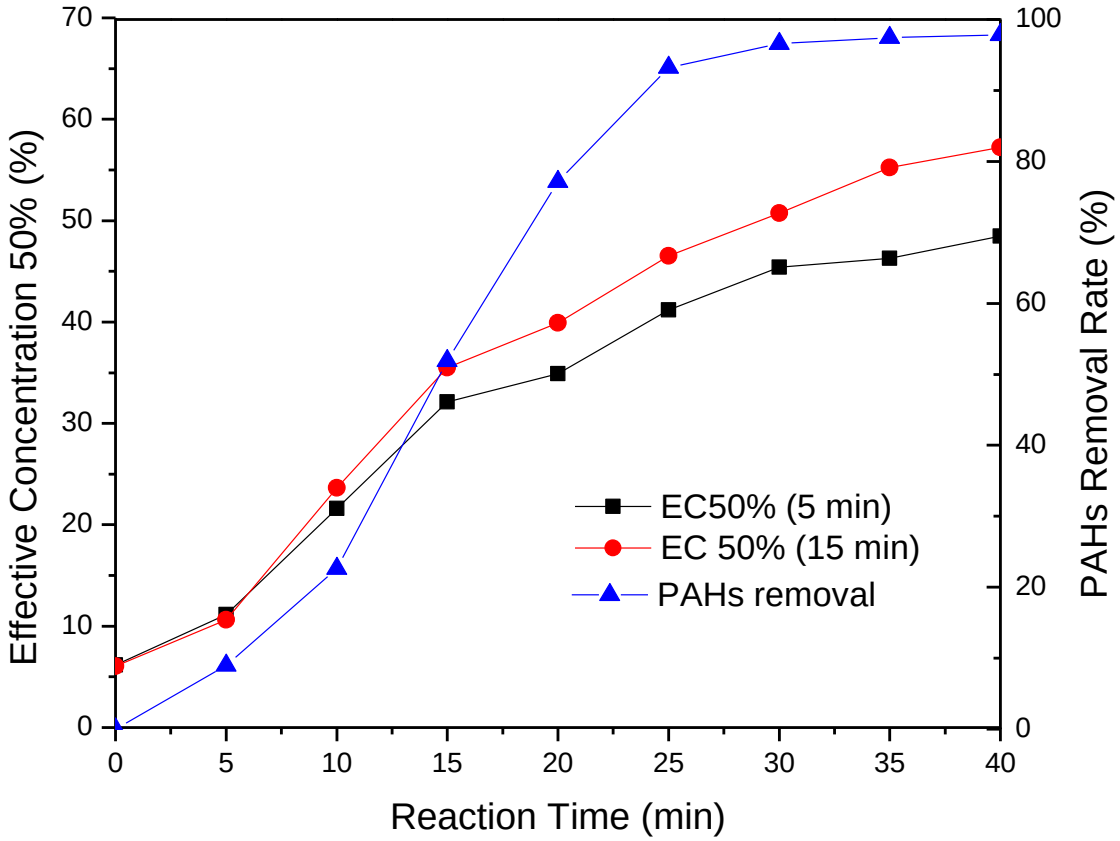


Figure 5.27 The relationship between toxicity (EC_{50}) and removal of PAHs (ozone dose = 10 ppm)

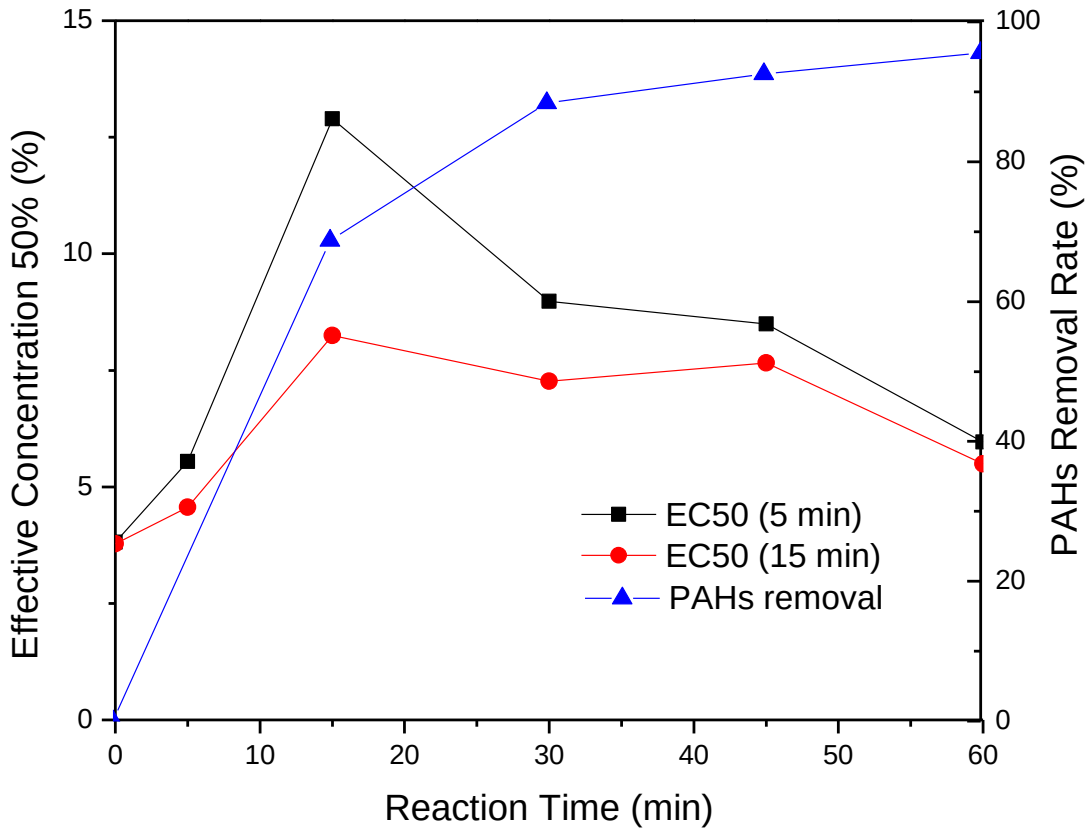


Figure 5.14 EC_{50} changes of produced water at the ozone dose of 20 ppm

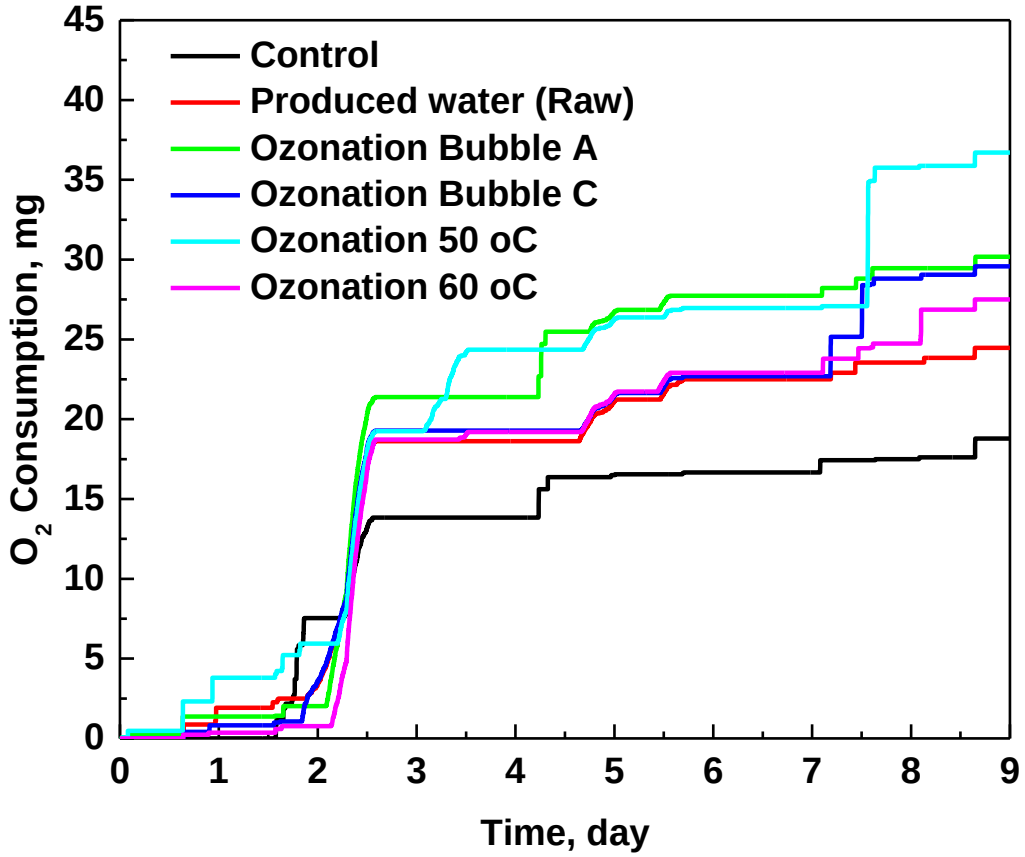


Figure 5.29 Oxygen uptake of different offshore produced water samples

Table 5.7 O_2 uptake, BOD, COD and removal ratio by biodegradation

OPW sample	O_2 Uptake mg/L (7 days)	BOD	COD	Removal ratio (BOD/COD)
OPW (raw)	11.6706	0.116706	1.551	7.52
Ozonation - Bubble size A	22.1422	0.221422	1.250	17.71
Ozonation - Bubble size C	12.0562	0.120562	1.184	10.18
Ozonation - 50 ºC	20.5978	0.205978	1.217	16.93
Ozonation - 60 ºC	12.4868	0.124868	1.150	10.86

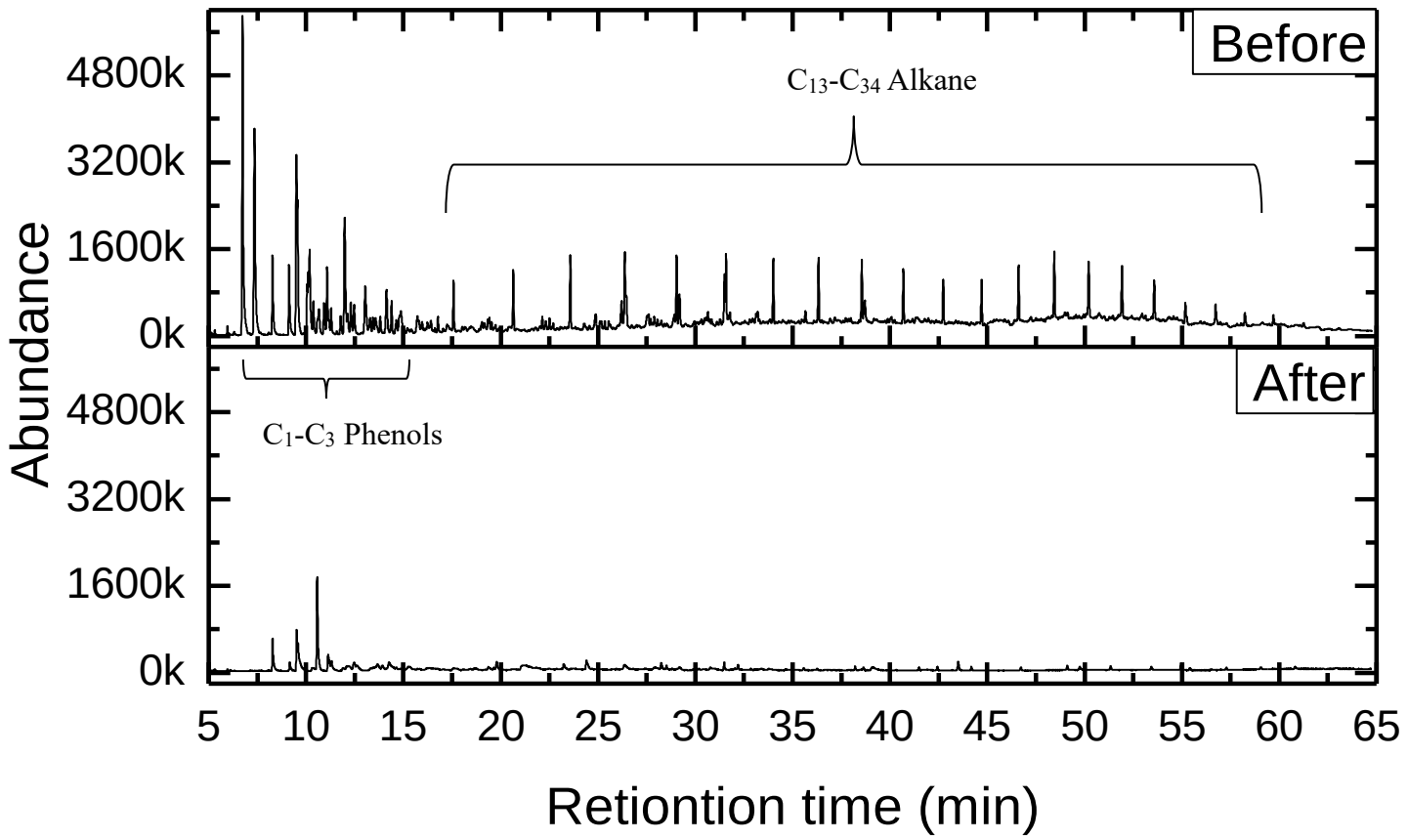


Figure 5.30 The changes of TIC chromatograms caused by biodegradation

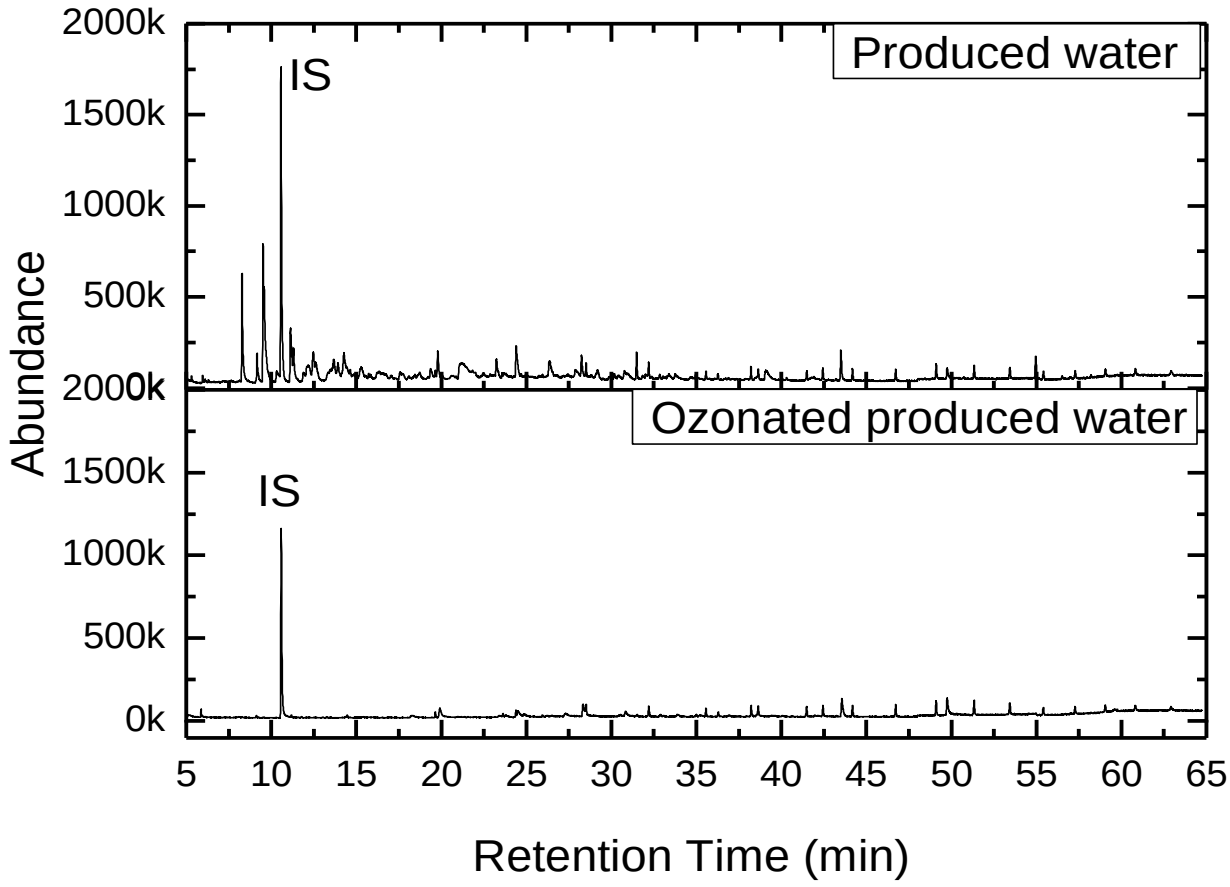


Figure 5.15 Comparison of organic residues in OPW and ozonated OPW after biodegradation

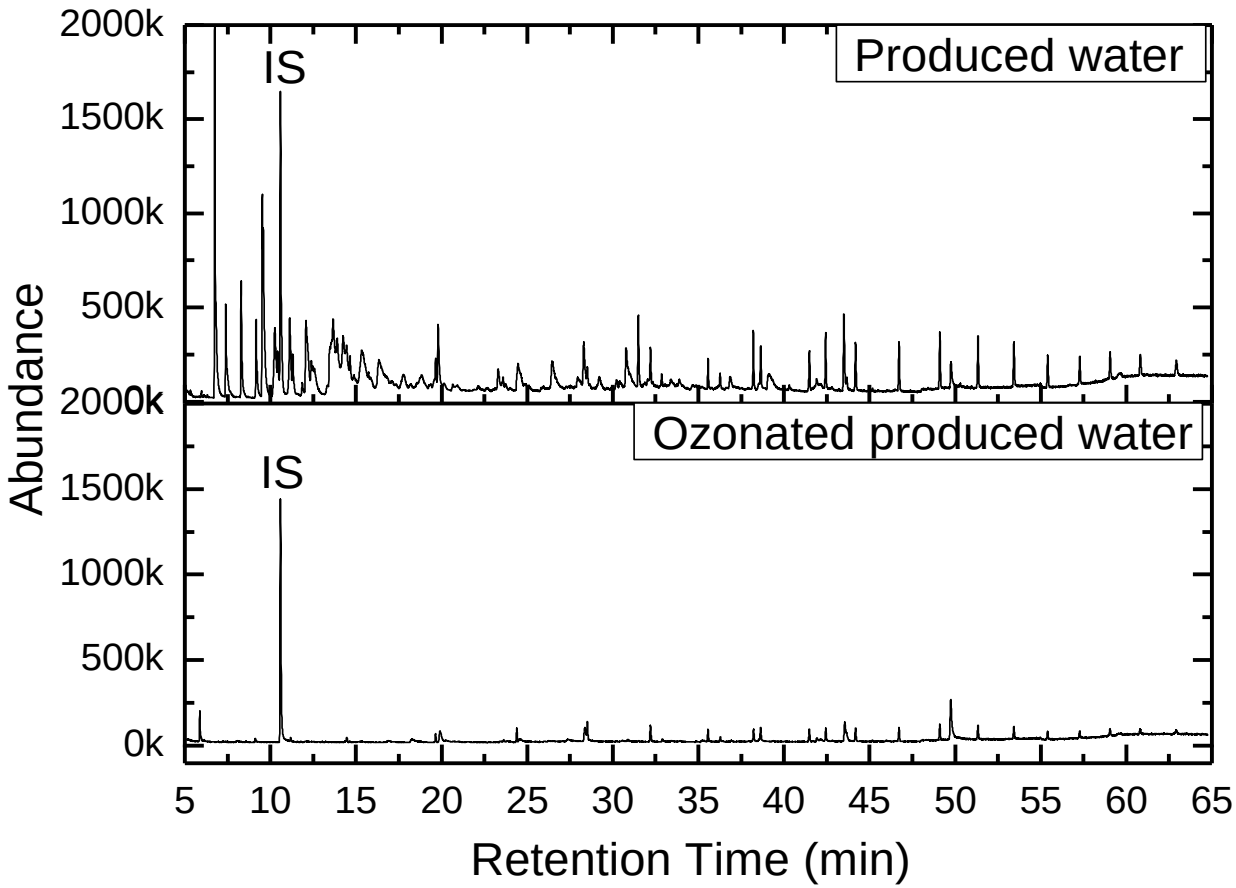


Figure 5.16 Comparison of organic residues in OPW and ozonated OPW after biodegradation with the presence of low DOC seawater

Like photolysis, ozonolysis also has high selectivity. The difference is that the ozonolysis usually convert compounds into less reactive species, leading to a rapid decrease of competitiveness. Since the reactions of ozone is more intense, the dynamic of competitiveness of ozone is stronger than that of photolysis. Though the molar reactivity of PAHs is relatively high, the initial concentration of PAHs is too low to compete for ozone with other reactive species (Phenol, BTEX, and halides). The low initial competitiveness of PAHs leads retards the removal rate at the initial stage. Only after a period of treatment, the concentration of species with higher competitiveness is reduced, and then the degradation of PAHs is accelerated (**Section 5.3**).

The hydroxyl radical is a universal oxidant with very low selectivity for organic compounds. More species can compete for this oxidant with PAHs. Therefore, the pathway involving it showed a non-significant effect on the experimental results. Virtually, in the case of low pH ozonation, the reduction of competitiveness of OH^- significantly enhanced the ozonolysis of PAHs. In contrast, the high pH value which promoted the hydroxyl radical generation did not show any positive effect on the removal of PAHs. However, the competition does not only exist for oxidants between target pollutants and the substrate, but also effect the generation of hydroxyl radicals. The reduction of substrate competitiveness for ozone can lead to an enhancement of hydroxyl radical formation in the late period of treatment, thus accelerating the destruction of dispersed oil and PAHs.

5.4.2 Radical Induced Synthesis

During UV irradiation and ozonation, the hydroxyl radicals and photons can convert the organic compounds into their radical forms, as the following reaction shows,

$$R(H) + hv \rightarrow R(H)^+ \cdot + e^- \rightarrow R \cdot + H^+ + e^-$$

$$R(H) + OH \cdot \rightarrow R \cdot + H_2O$$

Where R is the organic compound and R· is its radical form. Certain kinds of R·, for example, the olefins, can initiate the chain reactions inducing polymerization:

$$R \cdot + R \rightarrow R - R \cdot$$

Since this chain reaction does not consume any radical initiator, the reaction can be very rapid. Therefore, certain polymerized organic compound can be formed in short time. However, the olefins are rarely present in offshore produced water, so this pathway might not be considered.

On the other hand, the organic radicals can bond to each other by the radical reaction:

$$R \cdot + R \cdot \rightarrow R - R$$

For photolysis, the radical can be generated by the most of the aromatic compounds including PAHs, benzenes, BETX and other compounds with aromatic structure. In the case of hydroxyl radical reaction, most organic species can be converted to their radical forms. Therefore, after the radicals bond each other to form large organic molecules, the products can be further converted to radicals and bond to other radicals. The molecular size thus keeps growing through a serious of the radical propagation. It should be noticed that oxygen can also be a competitor of R· through the following reaction:

$$R \cdot + O_2 \rightarrow ROO \cdot$$

In cases of deionized water, drinking water and other cleaner water, due to the higher concentration of oxygen and lower concentration of organic pollutants, the R· has low competitiveness for R·+R· reaction. Therefore, the polymerization effect is usually

insignificant and not considered. Most R· reacted with oxygen to be rapidly oxidized, resulting in a high efficiency of COD reduction. In the case of a wastewater or produced water, the deoxygenated conditions and high concentrations of organic compounds may take place in the treatment process. Because of the high concentration of organic compounds and high generation rates of oxidants, a high concentration of organic radicals can be achieved under such conditions, resulting in a much greater competitiveness of R· while lower competitiveness of oxygen due to reduced concentration. The R·+R· reactions are therefore significantly enhanced, and the ROO· generation is inhibited. This mechanism can also be a reason for that the COD reduction rates by AOP are reported to be much more retarded in wastewater treatment than in drinking water.

When a significant amount of large organic molecules are formed, more insoluble compounds may be presented in offshore produced water to form dispersed oil film or droplets. This phenomenon was observed in both photolysis and ozonation process. The formed dispersed oil can absorb the PAHs and protect them from oxidants in water thus retard the removal rates. In the case of ozonation, the dispersed oil layer and droplets were destructed in late period especially when UV are introduced to enhance the hydroxyl radical reaction. This result is because that the number of organic molecules is reduced due to their bonding with each other and the concentration of R· is reduced. Also, the R·-R· reactions may also lead to the formation of PAHs although the specific substrates for these reactions are still unknown. This hypothesis can explain the increase of concentration for PAHs.

5.4.3 Halogenation

In offshore produced water, halides are presented as dominant inorganic species.

Therefore, halides usually have high competitiveness for oxidants. In photolysis, the iodide ion can be converted to the radicals. In the case of ozonation, the chloride, bromide and iodide are all able to transform into their more oxidative forms. These reactions are listed below:

$$Cl^- + OH\cdot \rightarrow [HOCl]^-\cdot$$

$$[HOCl]^-\cdot + H^+ \rightarrow Cl\cdot + H_2O$$

$$Br^- + OH\cdot \rightarrow Br\cdot + OH^-$$

$$I^- + OH\cdot \rightarrow I\cdot + OH^-$$

$$R + hv \rightarrow R^+\cdot + e^-$$

$$I^- + R^+\cdot \rightarrow I\cdot + R$$

$$X^- + O_3 \rightarrow XO^- + O_2$$

$$XO^- + X^- + 2H^+ \rightarrow X_2 + H_2O$$

$$XO^- + hv \rightarrow X\cdot + O^-\cdot$$

$$X_2 + hv \rightarrow 2X\cdot$$

Where X refers to different kinds of halide element. Through these reactions, the major oxidative products are X_2 and X atomic radicals (X·). These species can be involved in the treatment process by the following reactions:

$$X_2 + R(H) \rightarrow RX + HX$$

$$X_2 + R\cdot \rightarrow RX + X\cdot$$

$$X\cdot + R\cdot \rightarrow RX$$

By these reactions, the halides in offshore produced water can cause halogenation reactions. The halogenated organic compounds are thus found as the by-products of AOP

treatment of offshore produced water. A proof for this is that the trihalomethanes were identified as the by-products of ozonation described in the **Section 5.3.2**. However, these C-X bond can be further attacked by hydroxyl radicals for OH-substitution form alcohols, allowing to reduce the toxicity, indicating the significance of hydroxyl radical reaction.

5.5 Toxicity and Biodegradability

5.5.1 Toxicity Analysis

Ozonation was more efficient in the degradation of unsaturated organic compounds such as olefins and aromatic hydrocarbons. Phenols were oxidized by hydroxyl radicals and the formation of by-products in different ozonation stages was proved: muconic acid was the initial product; catechol, hydroquinone, fumaric acid, maleic acid were the intermediate products. Oxalic and formic acids accumulated with the ozonation time, and there were basic final products. PAHs had similar pathways. PYR for example reacted with ozone to form an aldehyde, carboxylic acids, and dialdehyde. Moreover, dialdehyde was further degraded by the loss of aldehydes group (CHO-) and the open of aromatic ring. In the final stage, a trace level of oxalic and formic acids could be observed. These findings echoed some results reported previously although most studies were not produced water related (Von Gunten, 2003a; Poznyak and Vivero, 2005; Choi and Hong, 2007). When reacting with nature organic matter (NOM), the ozonated by-products, such as aldehydes, ketones, ketoaldehydes, carboxylic acids, keto acids, hydroxyl acids, alcohols, and esters were reported (Von Gunten, 2003a). The EC_{50} values of these compounds decreased with

increasing chain length of the C_1-C_7 acids (Chou and Hee, 1992).

Produced water contained significant amounts of iodide, bromide, and chloride that can react with ozone. The generation of oxidative acids and halogenated organic compounds would increase the acute and chronic toxicity of the samples (Von Gunten, 2003b). Huang et al. evaluated the effect of ozonation to the acute toxicity and mutagenic property of ground water containing bromide (Huang *et al.*, 2009). The concentration of bromide in ground water and the generation of by-products (bromoform and bromate) were linearly correlated with the acute toxicity. As the concentration of bromide was 2.38 mg/L, the EC_{50} of the ozonated water sample dropped from 53% to 11%. The background concentration of bromide in produced water was from 89.3 mg/L to 93.56 mg/L. It was much higher than the literature. The high concentration of bromoform was also reported in the previous Chapter, indicating that these by-products were the key factors contributing to the decrease of EC_{50}.

Ozone can react with variable toxic organic compounds such as PAHs in offshore produced water. Consequently, the acute toxicity of treated produced water could be reflected by the degradation of toxic parent compounds and the generation of ozonated by-products such as disinfection by-products (DBPs). When ozone dose was a limiting factor, the acute toxicity of produced water samples was strongly related to their PAHs and phenols' concentrations. **Table 5.6** in page 201 lists the EC_{50} (5 min) values for the individual compounds. As suggested by Wells at al. (Wells *et al.*, 1997), the toxicity values of most PAHs were low than 1 mg/L, in which ANY had a lowest one of 0.34 mg/L, Phenol had a much higher EC_{50} value than PAHs, indicating the lower toxicity and concern regarding environmental impacts.

As discussed before, phenols have a similar degradation trend with PAHs in the ozonation process. Thus, the total removal of PAHs could represent the total removal of PAHs and Phenols. As shown in **Figure 5.31**, the EC_{50} was increased from a dilution rate of 6% to 70%-81%, suggesting a good correlation between the removal of PAHs and the acute toxicity of treated produced water. The significantly reduced toxicity present high value of the technique to offshore produced water management. However, the results with higher ozone dose show a different pattern (**Figure 5.32**). The EC_{50} increased first and then decreased due to the overdosed ozone concentration since the enhanced halogenation effect. This result indicates that the process should be optimized in toxicity aspects and should concern about the halogenation process.

5.5.2 Biodegradability Analysis

The effect of ozonation on the biodegradability of offshore produced water was evaluated by the oxygen uptake experiment in 7 days. As shown in **Figure 5.33**, the oxygen consumption of all the offshore produced water samples was at least 6 mL higher than that of the control sample (50 mL distilled water + 450 mL seawater with nutrient). The decrease of transparency was observed due to the growth of bacteria. Ozonated offshore produced water had the shortest period (<18 h) to lose transparency, followed by untreated offshore produced water (<24 h) and finally the control samples (around 48 h). It was implied that ozonated offshore produced water was much less toxic than untreated offshore produced water and contained more biodegradable organics as compared with the control samples. The addition of carbon source could enhance the consumption of oxygen because of the limited dissolved carbon in the fresh seawater (3.77 mg DOC/L). The enhancement of

ozonation towards biodegradability could be obviously observed. Offshore produced water sample had a 7-day oxygen consumption of 22.5 mL, meanwhile the highest values could reach 27.74 mL and 26.97 mL under two controlling conditions of bubble size (A - green line) and temperature (50 ^{o}C - cyan line), respectively.

The oxygen uptake, BOD, and COD values were tabulated in **Table 5.7**. It was indicated that ozonation increased the oxygen uptake of offshore produced water compared with untreated one. Especially for ozone bubble size A (1.11 mm, room temperature) when using diffuser A, the ozonated offshore produced water was able to uptake 22.1 mg/L oxygen, which was twice as much as the oxygen uptake of the untreated offshore produced water. Therefore, the increase of biodegradability of offshore produced water by ozonation was significant. The reasons could be explained from two aspects: 1) The removal of PAHs and phenols could significantly reduce the toxicity of offshore produced water thus increase the activity of microorganisms (reflected in the increase of O_2 uptake and BOD and the decrease of COD). PAHs with 1, 2 and 3 rings are acutely toxic while higher molecular weight PAHs are genotoxic (Gupta *et al.*, 2015). The presence of the phenolic compound could increase in lag (acclimation) and decrease the rate of degradation. 2) Ozonation also can transform the less biodegradable organics into the higher ones. The organic by-products such as aldehydes, ketones, keto aldehydes, carboxylic acids, keto acids, hydroxy acids, alcohols, and esters are readily biodegradable and may lead to an increase in the concentration of the assailable organic carbon (Von Gunten, 2003a). The removal ratio of BOD to COD was also increased significantly, although it might be compromised by the existence of a significant amount of reductive inorganic components and non-degradable organic matter in offshore produced water. It also indicated the need for examining the

influence of such compounds on the treatment efficiency in future research.

The DOC tests were to investigate the overall removal of dissolved organic compounds in offshore produced water after 7 days degradation. Considerable amounts of DOC in offshore produced water (10.6-13.0 mg/L) were removed after biodegradation compared with the control sample. However, the degradation of organics (10.6-13.0 mg/L) in all the offshore produced water samples, regardless of their concentrations, was like others. It was implied that the ozonation had a negligible effect on biodegradability and the system reached its capacity of degradation. The initial DOC concentration of offshore produced water ozonated at 60 ^{o}C was the lowest compared with all the other ozonated samples and associated DOC removal by biodegradation was highest (13 mg/L). The mineralization rates were calculated by the ratio of the deducted DOC to the initial DOC concentrations. For ozonated offshore produced water with Bubble Size A, Bubble Size C, offshore produced water after ozonated at 50 ^{o}C and 60 ^{o}C, the mineralization rates were 59.7%, 56.3%, 29.7% and 74.0%, respectively. It was suggested that the organic carbon in offshore produced water was partly mineralized. The residue of DOC could be the intermediates of biodegradation and ozonation. The mechanisms for the aerobic bacterial metabolism of PAHs are the initial oxidation of the benzene ring by the action of dioxygenase enzymes to form cis-dihydrodiols. These dihydrodiols are dehydrogenated to form dihydroxylated intermediates, which can further metabolized via catechols to carbon dioxide and water. The intermediates are initialized as protocatechuates, catechols, gentisates, homoprotoocatechuates, homogentistases, hydroquinones, hydroxyquinols, further to tricarboxylic acid cycle intermediates and the intermediates of kerb's cycle in the final stage (Gupta *et al.*, 2015). The main intermediates of the alkane degradation are fatty acids.

As reported by (Wells *et al.*, 1997), these acids could be further decomposed by the pathway typical of physiologica carboxylic acid degradation, in which the molecule is shortened stepwise.

Figure 5.34 illustrated the change of all the organic matter in offshore produced water after 8-day biodegradation without ozonation. Almost all the aliphatic hydrocarbons (C_{13} to C_{34}) were removed by the process, demonstrating a higher effectiveness of biodegradation. These organic compounds tended to have higher biodegradability. Phenols and PAHs were more resistant to biodegradation due to their low bioavailability. The larger molecular weights of PAHs could reduce the accessibility of the PAHs for metabolism by the microbial cell (Gupta *et al.*, 2015). As shown in **Figure 5.34**, the residue of alkyl phenols (mainly C_1-C_3) can still be observed leading to the toxicity of the effluent. PAHs also showed a less removal rate during biodegradation. For example, around 22% NAP in offshore produced water remained after biodegradation.

Figure 5.35 compares the organic residue of offshore produced water and ozonated offshore produced water after biodegradation. Without ozonation, there were still some residues in the effluent even after 8-day biodegradation; on the contrast, with ozonation, the phenols and PAHs were significantly removed before biodegradation, leaving almost no residue observed after biodegradation. It indicated that after ozonation treatment of offshore produced water, the effluent would be easily degraded by bacteria in the ambient receiving water body. Therefore, it demonstrated the necessity and value of adopting ozonation for removal of PAHs and phenols to reduce toxicity in the offshore produced water effluent and to better protect ocean ecosystem.

Meanwhile, the biodegradation of offshore produced water was also affected by the

property of seawater. One of the factors is hydrocarbon-degrading bacteria widely distributed in marine habitats. For example, cyanobacteria, *Pseudomonas, Marinobacter, Alcanivorax, Microbulbifer, Sphingomonas, Micrococcus, Cellulomonas*, *Dietzia*, and *Gordonia* groups were proved for their capacity to degrade hydrocarbons. Many bacteria species, such as *alcanivorax, Cycloclasticus Marinobacter Neptunomonas Oleiphilus,* and *Oleispira* have been isolated for the degradation of alkanes or aromatic compounds. Bacteria can selectively degrade the hydrocarbons. For example, *Alcanivorax* strains grow on n-alkanes and branched alkanes. *Cycloclasticus* strains grow on the aromatic hydrocarbons, naphthalene, phenanthrene, and anthracene, whereas *Oleiphilus* and *Oleispira* strains grow on the aliphatic hydrocarbons, alkanols and alkanoates. The bacterial degradation of PAHs which composed of three rings has been well documented. The most commonly reported bacterial species include *Acinetobacter*, *Alcaligens, Mycobacterium* sp., *Pseudomonas, Rhodococcus* sp., *Corynebacterium renale, Moraxella*sp., *Bacilluscereus, Micrococcus* sp., *Pseudomonas, paucimobilis*, and *Sphingomonas*sp. (Wells *et al.*, 1997; Gupta *et al.*, 2015).

Alcanivorax, *Cycloclasticus Rhodococcus, and Bacillus* were found in Newfoundland marine region and were cultured from oil contaminated samples (Yakimov *et al.*, 2007). It was believed that these species played a key role in biodegradation. As the DOC concentration of seawater decreased from 3 to 1 mg/L, the available biota community might be less in seawater before the biodegradation. As the bioactivity of hydrocarbon-degrading bacteria in seawater became a critical factor, the toxicity of offshore produced water would significantly affect the biodegradation. The overall effectiveness is depicted in **Figure 5.36**, where the residue of ozonated offshore produced water after biodegradation included

bromoform (Retention time = 5 min), eicosenamide (Retention time = 50 min) and some esters. A higher response of these residues could be found in offshore produced water. Additionally, significantly concentrations of C_1-C_3 phenols were still observed. As compared with the seawater with higher DOC, the residue of NAP was increased from 22% to 70%. Therefore, the bioactivity of bacteria was suppressed. As indicated before, the removal of PAHs and Phenols by ozonation first resulting in more biodegradable compounds would be able to achieve a much higher effectiveness.

5.6 Summary

The dissolved fractions of oil in offshore produced water, such as polycyclic aromatic hydrocarbons (PAHs), are persistent in the environment and extremely toxic and possibly carcinogenic, owing to the stringent regulations imposed recently, a thorough treatment of offshore produced water must be carried out before discharge. Aside from physical separation technologies that can deal with free oil and dispersed oil, ozonation has recently been gaining significant attention and regarded as a promising solution to remove dissolved hydrocarbons, especially PAHs. This study, therefore, targeted the removal of 16 US EPA priority PAHs from offshore produced water using ozonation. The effects of bubble size, ozone dose, pH, and temperature were studied using one-factor-at-a-time experiments. The toxicity and biodegradability of ozonated offshore produced water were also examined to provide insights into the feasibility and impacts of ozonation.

The results demonstrated that ozonation was an efficient technology for removing

PAHs in offshore produced water. The PAHs formation, induced polymerization and oxidation are the three fundamental mechanisms for ozonation or UV/ozone treatment of offshore produced water. It was found that smaller bubble size also showed a positive effect on the removal rates. Increased ozone dose was found to be effective at promoting the treatment efficiency. Lower pH could significantly increase removal efficiency by reducing the competition of substrate; while higher pH had lower efficiency due to increasing matrix reactivity caused by hydroxyl ions. A Higher temperature could decrease the efficiency. However, comparing to drinking water or municipal waste water, the high content of halides significantly inhibited the oxidation of target pollutants. On the other hand, the formation of oil film and droplets was also a major problem that slowed down the process by preventing resistant PAHs from water and ozone molecules. The formed oil film and suspended droplets during ozonation had an inhibition to extract the free dissolved PAHs.

Three major mechanisms of offshore produced water substrate affecting the PAH removal by AOP techniques are identified. These mechanisms include a dynamic competition of oxidants, radical induced organic synthesis, and halogenation. The dynamic competition majorly causes the significant change of degradation rate and errors ith conventional kinetic modeling. The radical induced synthesis effect is related to the dispersed oil formation which prevents the target pollutants from oxidants. It may also be related to the increase of PAHs' concentration as well. The halogenation can explain the formation of chlorinated organics which is a concern for the toxicity. These mechanisms are the first time promoted for wastewater treatment. The discovery of these mechanisms is not only valuable for understanding and analyzing PAHs removal in offshore produced water but also can help understanding the COD and toxicity reduction of wastewater

treatment. Although there are two models regarding the kinetics of dynamic competitiveness in photolysis and ozonation respectively developed in this study, the kinetics of the other two mechanisms remain unidentified, leading to a demand for further study.

Toxicity analysis results showed that ozonation could reduce the overall acute toxicity of offshore produced water. The EC_{50} was increased from a dilution rate of 6% to 70%-81% after 40 min ozonation, suggesting a good correlation between the removal of PAHs and the acute toxicity of treated offshore produced water. However, when increasing ozone dose to 20 ppm, EC_{50} was first increased to 13% after 15 min ozonation, and then decreased to 5% at the end. This result could be attributed to the fact that more ozone reacted with other substrates (e.g., iodide, bromide and chloride) and generated more toxic disinfection by-products. Therefore, an optimal control of ozone dose is crucial to the treatment performance while not increasing toxicity during the ozonation process. The biodegradability tests revealed a positive effect of ozonation on enhancing the biodegradation of offshore produced water, in which the oxygen consumption increased twice as much as untreated offshore produced water. Ozonation could remove the less biodegradable compounds (such as PAHs and phenols) which are also toxic to bacteria and generate more biodegradable organic products stimulating the growth of bacteria. The mineralization rates of the ozonated offshore produced water samples reached 74% leaving the residues consisting of the by-products of biodegradation and ozonation such as tricarboxylic acids and fatty acids. For untreated offshore produced water, the traceable amount of PAHs and phenols were still observed after the 7-day biodegradation tests. The results also suggested a promising option by applying ozonation and bioremediation

sequentially first to degrade or decompose the compounds with lower biodegradability like phenols and PAHs and then the more biodegradable ones to achieve overall high efficiency for offshore produced water treatment.

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary

Since discharge is one of the major options for offshore oil and gas industry to dispose produced water, the toxic organic pollutants (especially including polycyclic aromatic hydrocarbons or PAHs) in the produced water are of great environmental concerns due to the negative impacts on the marine and coastal environments if without proper treatment. Present treatment technologies and practices mainly focus on the removal of suspended and dispersed forms of those pollutants, which may leave dissolved but highly toxic compounds entering the oceans. Advanced oxidation processes (AOPs) are promising technologies which should be capable for effectively removing those pollutants with some favorable features such as high cost-efficiency, small footprints, and eco-friendliness especially suitable for offshore operations. However, due to the limited previous studies on offshore produced water treatment, the mechanisms, performance, and effectiveness of removal of PAHs by AOPs remain unknown. Therefore, this research was to make experimental and modeling efforts to help answer some important scientific questions and evaluate the capability of AOPs for offshore produced water treatment.

To develop a efficient exerimental methodology, an analytical method named Vortex-shaker Assisted Liquid-liquid Micro-extraction (VSA-LLME) was developed by this study to improve the characterization of offshore produced water. The parameters affecting the VSA-LLME performance including solvent volume, ion strength, extraction time and centrifuge speed were optimized. Under the optimized condition, the enrichment factors range from 68 to 78. The linearity results (R^2s) of the proposed methods for all 16 PAHs were above 0.99. The recoveries of the method were 74-85%, and the limits of detection

were as low as 2 to 5 ng/L. The relative standard deviations (RSD%s) were 6~11%. The developed method offers advantages including simplicity of operation, low cost, and high sensitivity showing a great potential for monitoring water samples containing PAHs in the marine environment.

Direct photolysis was investigated. The removal of trace organic pollutants shows more complicated kinetics than those in cleaner waters, which is due to the complex chemical constitutions of the substrate. The experimental results illustrated that the mechanisms including direct photolysis, dynamic light screening, and radical induced organic synthesis are affecting the removal process. A kinetic model involving dynamic light screening has been developed to aid the kinetic analysis, and a semi-empirical model has been drawn up to simulate the process. The model prediction showed good correlation with experimental results. However, the developed kinetic model has significant limitations since the PAHs' quantum yields are not constant in offshore produced water. Also, the radical induced synthesis effect may also significantly affect the concentration of PAHs. Although a semi-emperial model has been developed in this study with good correlation with experimental results, further studies focusing on understanding and simulating these mechanisms are demanded.

Aside from physical separation technologies that can deal with free oil and dispersed oil, ozonation has recently been gaining significant attention and regarded as a promising solution to remove dissolved hydrocarbons, especially PAHs. This study, therefore, targeted the removal of 16 US EPA priority PAHs from offshore produced water using ozonation. The effects of bubble size, ozone dose, pH, and temperature were studied using one-factor-at-a-time experiments. It was found that smaller bubble size also showed a positive effect

on the removal rates. Increased ozone dose was found to be effective at promoting the treatment efficiency. Lower pH could significantly increase removal efficiency by reducing the competition of substrate; while higher pH had lower efficiency due to increasing substrate reactivity due to hydroxyl ions. A Higher temperature was observed to decrease the efficiency. The toxicity and biodegradability of ozonated offshore produced water were also examined to provide insights into the feasibility and impacts of ozonation. The results demonstrated that ozonation was an efficient technology for removing PAHs in offshore produced water. The three major substrate impact mechanisms were then identified. These mechanisms include a dynamic competition of oxidants, radical induced organic synthesis, and halogenation. These mechanisms illustrated in this study are the first timely proposed for wastewater treatment. The discovery of these mechanisms is not only valuable for PAHs removal in offshore produced water, but also can help understanding the COD and toxicity reduction of wastewater treatment. Although there are two models regarding the kinetics of dynamic competitiveness in photolysis and ozonation respectively developed in this study, the kinetics of the other two mechanisms remain unidentified, leading to a demand for further study. The EC_{50} was increased from a dilution rate of 6% to 70%-81% after 40 min ozonation, revealing a good correlation between the removal of PAHs and the acute toxicity of treated offshore produced water. However, when increasing ozone dose to 20 ppm, EC_{50} was first increased to 13% after 15 min ozonation, and then decreased to 5% at the end. This result could be attributed to the fact that more ozone reacted with other substrates (e.g., iodide, bromide and chloride) and generated more toxic disinfection by-products. The biodegradability tests revealed a positive effect of ozonation on enhancing the biodegradation of offshore produced water, in which the oxygen consumption increased

twice as much as untreated offshore produced water. Ozonation could remove the less biodegradable compounds (such as PAHs and phenols) which are also toxic to bacteria and generate more biodegradable organic products stimulating the growth of bacteria. The mineralization rates of the ozonated offshore produced water samples reached 74% leaving the residues consisting of the by-products of biodegradation and ozonation such as tricarboxylic acids and fatty acids.

6.2 Research Contributions

The major research contributions can be summarized from the following aspects:

1) **Sample analysis – VSA-LLME Method**

   A novel VSA-LLME method for determination of 16 priority PAHs in offshore produced water has been developed. This method utilizes the constitutes in produced water as dispersive solvents, and can significantly increase the detective efficiency with low cost, straightforward procedure, less solvent consumption and high analytical performance. It provides a fast, reliable method of offshore wastewater sample analysis for not only research purpose but governmental and industrial practice.

2) **Photolysis and ozonation – approved options for OPW treatment and PAHs removal**

The photolysis has been approved to be an efficient option to remove PAHs from offshore produced water. The efficiency majorly relate to the irradiance intensity, light screening of produced water, and the exitinction coefficients of the PAHs. Ozonation has been investigated to be a more efficient technology. Direct ozonlysis was indientified to the major mechanism to oxidize PAHs. The treatment by-products of offshore produced water ozonation are identified to be halogenated organic compounds. Although these by-products can be further transformed to less-toxic species by AOPs, the low-cocnetration residue can cause chronic impact to eco-system. This result demonstrated a new concern that insufficient AOPs treatment can lead to a chronic impact to eco-system, indicating the importance to apply optimized AOPs. The effects of the major operational factors are identified. The results demonstrated that the factors can cause different effects in offshore produced water than that of in clean water. These results can assist engineers to understand and design the produced water treatment practice.

3) **Photolysis and ozonation – new mechanisms and novel kinetic modelings**

The major mechanisms affecting the PAHs removal through AOP treatment from produced water substrate were then identified. These mechanisms include a dynamic competition of oxidants, radical induced organic synthesis, and halogenation. These mechanisms are the first timely proposed for wastewater treatment, and can help to understand the oxidation behavior of PAHs and identify the effects of produced water substrate.

A novel kinetic model for the photolysis of PAHs in offshore produced water introducing dynamic light screening has been developed. This model shows better

correlation with experimental results than that of conventional first-order kinetic, which can help to achieve better investigation and understanding on the degradation process. A semi-empirical model for the photolysis of PAHs in offshore produced water derived from the previously developed kinetic model has been invented. This model innovatively introduced finite element concept to simulate the complex dynamic of light screening effect. The model provided a good correlation with experimental results and the a R^2 of 0.8468. The result can demonstrate that this model can accurately simulate the complicated PAH removal process in offshore produced water substrate.

Sequentially, a novel kinetic model based on dynamic oxidant competitiveness for ozonolysis of 16 PAHs in offshore produced water has been developed. This model can help to identify and quantify the effects of different operational parameters and simulate the treatment process.

4) **Toxicity and biodegradability – approved toxicity reduction and potential to be integrated with biodegradation**

Toxicity of the treated offshore produced water was evaluated to be reduced, and biodegradability was evaluated to be enhanced after AOP treatment. These results demonstrated the significance of this technology in offshore produced water treatment and its potential to combine with conventional wastewater treatment.

6.3 Publications

Journal Papers

Jisi Zheng, Bing Chen, Worakanok Thanyamanta, Kelly Hawboldt, Baiyu Zhang, Bo Liu: *Offshore produced water management: A review of current practice and challenges in harsh/Arctic environments*. Marine Pollution Bulletin 01/2016; 104(1). DOI:10.1016/j.marpolbul.2016.01.004

Jisi Zheng, Bo Liu, Jing Ping, Bing Chen, Hongjing Wu, Baiyu Zhang: *Vortex- and Shaker-Assisted Liquid–Liquid Microextraction (VSA-LLME) Coupled with Gas Chromatography and Mass Spectrometry (GC-MS) for Analysis of 16 Polycyclic Aromatic Hydrocarbons (PAHs) in Offshore Produced Water*. Water Air and Soil Pollution 09/2015; 226(9). DOI:10.1007/s11270-015-2575-3

Liang Jing, Bing Chen, Baiyu Zhang, Jisi Zheng, Bo Liu: *Naphthalene degradation in seawater by UV irradiation: The effects of fluence rate, salinity, temperature and initial concentration*. Marine Pollution Bulletin 04/2014; 81(1). DOI:10.1016/j.marpolbul.2014.02.003

Pu Li, Bing Chen, Baiyu Zhang, Jing Liang, Jisi Zheng: *Monte Carlo simulation-based dynamic mixed integer nonlinear programming for supporting oil recovery and devices allocation during offshore oil spill responses*. Ocean & Coastal Management 03/2014; 89. DOI:10.1016/j.ocecoaman.2013.12.006

Pu Li, Bing Chen, Baiyu Zhang, Liang Jing, Jisi Zheng: *A multiple-stage simulation-based mixed integer nonlinear programming approach for supporting offshore oil spill recovery with weathering process*. Journal of Ocean Technology 12/2012; 7(4).

Liang Jing, Bing Chen, Baiyu Zhang, Pu Li, Jisi Zheng: *Monte Carlo Simulation–Aided Analytic Hierarchy Process Approach: Case Study of Assessing Preferred Non-*

Point-Source Pollution Control Best Management Practices. Journal of Environmental Engineering 10/2012; 139(5). DOI:10.1061/(ASCE)EE.1943-7870.0000673

B.Y. Zhang, J.S. Zheng, R.G. Sharp: *Phytoremediation in Engineered Wetlands: Mechanisms and Applications*. 12/2010; 2. DOI:10.1016/j.proenv.2010.10.142

Conference Proceedings

Jisi Zheng, Bo Liu, Bing Chen, Baiyu Zhang, Liang Jing, Yinchen Ma: *Ozonation and Enhancement Methods as Treatment Options for Offshore Produced Water*. 6th Annual Arctic Oil & Gas North America Conference, St. John's, NL, Canada; 04/2015

Yinchen Ma, Bing Chen, Baiyu Zhang, Bo Liu, Jisi Zheng: *Degradation of Benzo [a] Pyrene in Offshore Produced Water by Ultrasound Fenton Process*. Hong Kong International Conference on Engineering and Applied Science (HKICEAS 2014), Hongkong, China; 12/2014

Yinchen Ma, Bing Chen, Baiyu Zhang, Bo Liu, Jisi Zheng: *Degradation of Benzo [a] Pyrene in Oily Marine Wastewater using Ultrasonic Irradiation*. The 37th Arctic and Marine Oilspill Program (AMOP) Technical Seminar, Canmore, Canada; 06/2014

Bing Chen, Baiyu Zhang, Liang Jing, Bo Liu, Jisi Zheng, Yinchen Ma: *Removal of Polycyclic Aromatic Hydrocarbons (PAHs) from Offshore Produced Water Using Advanced Oxidation Processes*. 11th IWA Leading Edge Conference on Water and

Wastewater Technologies, Abu Dhabi, United Arab Emirates; 05/2014

Yinchen Ma, Bing Chen, Baiyu Zhang, Jisi Zheng, Bo Liu, He Zhang: *Fenton's Oxidation Process for Remediation of Produced Water Containing PAHs*. The Canadian Society for Civil Engineering (CSCE) 2014 Annual General Meeting and Conference and the 13th International Environmental Specialty Conference, St. John's, Canada; 05/2014

Jisi Zheng, Bing Chen, Baiyu ZHang, Zelin Li, Tong Cao, Bo Liu: *Ozonation of polycyclic aromatic hydrocarbons in offshore produced water—the effect of pH and ozone doses*. The IBC Energy's 5th Annual Arctic Oil & Gas North America Conference 2014, St. John's, Canada; 03/2014

Liang Jing, Bing Chen, Baiyu Zhang, Jisi Zheng: *The Effects of Salinity and Temperature on the Photolysis of Naphthalene Using UVC Irradiation*. The 36th AMOP Technical Seminar on Environmental Contamination and Response, Halifax, Canada; 06/2013

Bo Liu, Jisi Zheng, Bing Chen, Baiyu Zhang: *A preliminary study on nano-catalyst enhanced heterogeneous photo-degradation of polycyclic aromatic hydrocarbons (PAHs) in produced water*. The 36th Arctic and Marine Oilspill Program (AMOP) Technical Seminar on Environmental Contamination and Response, Halifax, Canada; 06/2013

Jisi Zheng, Bo Liu, Baiyu Zhang, Bing Chen: *Photo-oxidation of EPA priority 16 polycyclic aromatic hydrocarbons (PAHs) in offshore produced water*. International Water Association (IWA) Leading-Edge Conference on Water and Wastewater Technologies (LET), Bordeaux, France; 06/2013

Bo Liu, Jisi Zheng, Bing Chen, Baiyu Zhang, Tong Cao: *An experimental study on the matrix effect of marine oily wastewater on nano-catalyst enhanced heterogeneous photo-degradation of polycyclic aromatic hydrocarbons*. IBC Energy's 4th Annual Conference - Arctic Oil & Gas North America 2013, St. John's, Canada; 04/2013

Jisi Zheng, Jing Ping, Z.Y. Li, Bing Chen, Baiyu Zhang: *Advanced oxidation of 16 polycyclic aromatic hydrocarbons (PAHs) in offshore produced water*. IBC Energy's 4th Annual Conference - Arctic Oil & Gas North America 2013, St. John's, Canada; 04/2013

Jing Ping, Z.Y. Li, Bing Chen, Jisi Zheng, Bo Liu, Baiyu Zhang: *Direct photolysis on polycyclic aromatic hydrocarbons (PAHs) in offshore produced water*. The 5th Canadian Wastewater Management Conference & 48th Central Canadian Symposium on Water Quality Research, Hamilton, Canada; 03/2013

Liang Jing, Bing Chen, Baiyu Zhang, Jisi Zheng, Pu Li: *A Stochastic Analytical Hierarchy Process for Supporting Nonpoint Source Pollution Control*. The 2012 Canadian Society for Civil Engineering Annual Conference, Edmonton, Canada; 06/2012

Jisi Zheng, Bo Liu, Jing Ping, Baiyu Zhang, Bing Chen: *Two analytical methods for real-time monitoring of polycyclic aromatic hydrocarbons in oil contaminated seawater*. The 35th Arctic and Marine Oilspill Program (AMOP) Technical Seminar on Environmental Contamination and Response, Vancouver, Canada; 06/2012

Pu Li, Bing Chen, Baiyu Zhang, Liang Jing, Jisi Zheng: *Development of a Multi-stage Simulation Based Mixed Integer Nonlinear Programming Approach for Supporting Offshore Oil Spill Recovery*. The 35th AMOP Technical Seminar on Environmental

Contamination and Response, Vancouver, Canada; 06/2012

Bo Liu, Jing Ping, Jisi Zheng, Baiyu Zhang, Bing Chen: *A review of mechanisms and photoproducts of polycyclic aromatic hydrocarbons (pahs) photo-oxidations*. The 64th Canadian Water Resources Association (CWRA) National Conference, St. John's, Canada; 06/2011

Jing Ping, Jisi Zheng, Baiyu Zhang, Kenneth Lee, Tahir Husain, Bing Chen: *Gas chromatography – mass spectrometry analysis of polycyclic aromatics hydrocarbons (PAHs) in offshore produced water*. The 64th Canadian Water Resources Association (CWRA) National Conference, St. John's, Canada; 06/2011

Jing Ping, Bing Chen, Jisi Zheng, Bo Liu, Baiyu Zhang: *A preliminary study on the ultraviolet irradiation effect on degradation of polycyclic aromatic hydrocarbons in offshore produced Water*. The 10th Specialized Conference on Small Water and Wastewater Treatment Systems of International Water Association (IWA), Venice, Italy; 04/2011

6.4 Recommendations for Future Research

1) There are different kinds of advanced oxidation technologies. The UV and ozone treatment are only two basic components. The other technologies have different oxidative mechanisms such as Fenton, UV/H_2O_2, photo-catalysis, and catalyzed ozonation may pose different kinetics. Aside from the PAHs, COD, APs and other pollutants can also cause significant environmental impact. Therefore, the research

may expand to more advanced oxidation technologies and more pollutants in offshore produced water.

2) AOPs show much more complexity in offshore produced water. Aside from the three mechanisms proposed in this research, there could be other interactions between the water substrate and the oxidant. In addition, among the proposed three mechanisms, the kinetics of radical induced synthesis and halogenation have not been developed. So, further study can be demanded to investigate such mechanisms and kinetics in wastewater treatment.
3) There are four operational factors examined in this research. The mechanism of how the temperature posed negative effect remains unknow. Further study may focus on this area. In addition, the operational factors are not limited in those four examined in this research. The other factors such as gas flowrate, gas velocity, UV type, water level height can also affect the removal based on the developed kinetic models. Further research may expand to more comprehensive factors to investigate the kinetics.
4) Sequential advanced oxidation and biodegradation provided high-performance collaboration in this research. Further study may be conducted to investigate the mechanisms and kinetics of their collaboration.

REFERENCES

Adewumi, M., Erb, J., & Watson, R. (1992). Initial Design Considerations for a Cost Effective Treatment of Stripper Oil Well Produced Water *Produced Water* (pp. 511-522): Springer.

Al-Muntasheri, G.A., Hussein, I.A., Nasr-El-Din, H.A., & Amin, M.B. (2007). Viscoelastic properties of a high temperature cross-linked water shut-off polymeric gel. *Journal of Petroleum Science and Engineering, 55*(1), 56-66.

Al-Muntasheri, G.A., Sierra, L., Garzon, F.O., Lynn, J.D., & Izquierdo, G.A. (2010). Water Shut-off with polymer gels in a high temperature horizontal gas well: A success story. Conference proceedings, SPE Improved Oil Recovery Symposium.

Aliaga, C., Park, J.Y., Yamada, Y., Lee, H.S., Tsung, C.-K., Yang, P., & Somorjai, G.A. (2009). Sum frequency generation and catalytic reaction studies of the removal of organic capping agents from Pt nanoparticles by UV− ozone treatment. *The Journal of Physical Chemistry C, 113*(15), 6150-6155.

Alkhudhiri, A., Darwish, N., & Hilal, N. (2013). Produced water treatment: Application of Air Gap Membrane Distillation. *Desalination, 309*, 46-51.

Altare, C.R., Bowman, R.S., Katz, L.E., Kinney, K.A., & Sullivan, E.J. (2007). Regeneration and long-term stability of surfactant-modified zeolite for removal of volatile organic compounds from produced water. *Microporous and Mesoporous Materials, 105*(3), 305-316.

Alvares, A., Diaper, C., & Parsons, S. (2001). Partial oxidation by ozone to remove recalcitrance from wastewaters-a review. *Environmental Technology, 22*(4), 409-427.

Alzahrani, S., Mohammad, A.W., Hilal, N., Abdullah, P., & Jaafar, O. (2013). Comparative study of NF and RO membranes in the treatment of produced water—Part I: Assessing water quality. *Desalination, 315*, 18-26.

AMAP. (2007). Arctic Oil and Gas 2007.

Amini, S., Mowla, D., Golkar, M., & Esmaeilzadeh, F. (2012). Mathematical modelling of a hydrocyclone for the down-hole oil–water separation (DOWS). *Chemical Engineering Research and Design*, *90*(12), 2186-2195.

Anlauf, H. (2007). Recent developments in centrifuge technology. *Separation and Purification Technology, 58*(2), 242-246.

Antonopoulou, M., Evgenidou, E., Lambropoulou, D., & Konstantinou, I. (2014). A review on advanced oxidation processes for the removal of taste and odor compounds from aqueous media. *Water Res, 53*, 215-234.

Arthur, C.L., & Pawliszyn, J. (1990). Solid phase microextraction with thermal desorption using fused silica optical fibers. *Analytical chemistry*, *62*(19), 2145-2148.

Arthur, J.D., Langhus, B.G., & Patel, C. (2005). Technical summary of oil & gas produced water treatment technologies. *All Consulting, LLC, Tulsa, OK*.

Bachman, R., Harding, T., Settari, A.T., & Walters, D. (2003). Coupled simulation of reservoir flow, geomechanics, and formation plugging with application to high-rate produced water reinjection. Conference proceedings, SPE Reservoir Simulation Symposium.

Bader, M. (2007). Seawater versus produced water in oil-fields water injection operations. *Desalination*, *208*(1), 159-168.

Bakke, T., Klungsøyr, J., & Sanni, S. (2013). Environmental impacts of produced water and drilling waste discharges from the Norwegian offshore petroleum industry. *Mar Environ Res, 92*, 154-169.

Banerjee, R., Ghosh, B., Khilar, K., Boukadi, F., & Bemani, A. (2008). Field application of phenol formaldehyde gel in oil reservoir matrix for water shut-off purposes. *Energy Sources, Part A, 30*(19), 1779-1787.

Barker, A., & Jones, C. (2013). A critique of the performance of EIA within the offshore oil and gas sector. *Environmental Impact Assessment Review, 43*, 31-39.

Barth, T. (1991). Organic acids and inorganic ions in waters from petroleum reservoirs, Norwegian continental shelf: a multivariate statistical analysis and comparison with American reservoir formation waters. *Applied Geochemistry, 6*(1), 1-15.

Beltran, F., Ovejero, G., & Acedo, B. (1993). Oxidation of atrazine in water by ultraviolet radiation combined with hydrogen peroxide. *Water Res, 27*(6), 1013-1021.

Beltran, F.J., Ovejero, G., Garcia-Araya, J.F., & Rivas, J. (1995). Oxidation of polynuclear aromatic hydrocarbons in water. 2. UV radiation and ozonation in the presence of UV radiation. *Industrial & Engineering Chemistry Research, 34*(5), 1607-1615.

Beltrán, F.J., Ovejero, G., & Rivas, J. (1996). Oxidation of Polynuclear Aromatic Hydrocarbons in Water. 3. UV Radiation Combined with Hydrogen Peroxide. *Industrial & Engineering Chemistry Research, 35*(3), 883-890.

Beltrán, F.J., González, M., & González, J.F. (1997). Industrial wastewater advanced oxidation. Part 1. UV radiation in the presence and absence of hydrogen peroxide. *Water Res, 31*(10), 2405-2414.

Beltrán, F.J., Rivas, J., Álvarez, P.M., Alonso, M.A., & Acedo, B. (1999). A kinetic model for advanced oxidation processes of aromatic hydrocarbons in water: application to phenanthrene and nitrobenzene. *Industrial & Engineering Chemistry Research, 38*(11), 4189-4199.

Bhadja, P., & Kundu, R. (2012). Status of the seawater quality at few industrially important coasts of Gujarat (India) off Arabian Sea. *Indian Journal of Geo-Marine Sciences, 41*(1), 90-97.

Bilstad, T., & Espedal, E. (1996). Membrane separation of produced water. *Water Science and Technology, 34*(9), 239-246.

Bird, K.J., Charpentier, R.R., Gautier, D.L., Houseknecht, D.W., Klett, T.R., Pitman, J.K., Moore, T.E., Schenk, C.J., *et al.* (2008). Circum-Arctic resource appraisal: Estimates of undiscovered oil and gas north of the Arctic Circle: Geological Survey (US).

Boese, B., Lamberson, J., Swartz, R., Ozretich, R., & Cole, F. (1998). Photoinduced toxicity of PAHs and alkylated PAHs to a marine infaunal amphipod (Rhepoxynius abronius). *Archives of Environmental Contamination and Toxicology, 34*(3), 235-240.

Boitsov, S., Mjøs, S.A., & Meier, S. (2007). Identification of estrogen-like alkylphenols in produced water from offshore oil installations. *Mar Environ Res, 64*(5), 651-665.

Boschee, P. (2012). Handling Produced Water from Hydraulic Fracturing. *SPE Journal*.

Bowen, T.C., Noble, R.D., & Falconer, J.L. (2004). Fundamentals and applications of pervaporation through zeolite membranes. *Journal of Membrane Science, 245*(1), 1-33.

Boyson, J., & Boyson, D. (2004). The Freeze-Thaw/Evaporation Process for Produced Water Treatment, Disposal and Benificial Use.

Braun, A.M. (2003). Photochemical Purification of Water and Air. By Thomas Oppenländer: Wiley Online Library.

Brendehaug, J., Johnsen, S., Bryne, K., Gjøse, A., Eide, T., & Aamot, E. (1992). Toxicity testing and chemical characterization of produced water—a preliminary study *Produced water* (pp. 245-256): Springer.

Bringedal, B., Ingebretsen, T., & Haugen, K. (1999). Subsea separation and reinjection of produced water. Conference proceedings, Offshore Technology Conference.

Broséus, R., Vincent, S., Aboulfadl, K., Daneshvar, A., Sauvé, S., Barbeau, B., & Prévost, M. (2009). Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment. *Water Res, 43*(18), 4707-4717.

Buffagni, M., Pinturier, L.M., Bracco, L., Moltu, U.E., Cova, C.A., & Jonsson, H. (2010). Environmental Risk Management of E&P Operations in the Barents Sea: environmental indicators and thresholds levels. Conference proceedings, SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production.

Burke, C., Montevecchi, W., & Wiese, F. (2012). Inadequate environmental monitoring around offshore oil and gas platforms on the Grand Bank of Eastern Canada: Are

risks to marine birds known? *Journal of environmental management, 104*, 121-126.

Bybee, K. (2005). A review of downhole separation technology. *Journal of Petroleum Technology, 57*(09), 48-50.

Çakmakce, M., Kayaalp, N., & Koyuncu, I. (2008). Desalination of produced water from oil production fields by membrane processes. *Desalination, 222*(1-3), 176-186.

Canonica, S., & Freiburghaus, M. (2001). Electron-Rich Phenols for Probing the Photochemical Reactivity of Freshwaters. *Environ Sci Technol, 35*(4), 690-695.

Canonica, S., Meunier, L., & Von Gunten, U. (2008). Phototransformation of selected pharmaceuticals during UV treatment of drinking water. *Water Res, 42*(1), 121-128.

CAPP. (2001). Produced Water Waste Management Technical Report.

Carls, M.G., Holland, L., Larsen, M., Collier, T.K., Scholz, N.L., & Incardona, J.P. (2008). Fish embryos are damaged by dissolved PAHs, not oil particles. *Aquat Toxicol, 88*(2), 121-127.

Casas, V., Llompart, M., García-Jares, C., Cela, R., & Dagnac, T. (2006). Multivariate optimization of the factors influencing the solid-phase microextraction of pyrethroid pesticides in water. *Journal of Chromatography A, 1124*(1), 148-156.

Casini, S., Marsili, L., Fossi, M., Mori, G., Bucalossi, D., Porcelloni, S., Caliani, I., Stefanini, G., *et al.* (2006). Use of biomarkers to investigate toxicological effects of produced water treated with conventional and innovative methods. *Mar Environ Res, 62*, S347-S351.

Casper, K.N. (2009). Oil and gas development in the Arctic: Softening of ice demands hardening of international law. *Nat. Resources J., 49*, 825.

Cha, Z., Lin, C.-F., Cheng, C.-J., & Hong, P.A. (2010). Removal of oil and oil sheen from produced water by pressure-assisted ozonation and sand filtration. *Chemosphere, 78*(5), 583-590.

Chang, I.-S., Chung, C.-M., & Han, S.-H. (2001). Treatment of oily wastewater by ultrafiltration and ozone. *Desalination, 133*(3), 225-232.

Charalabaki, M., Psillakis, E., Mantzavinos, D., & Kalogerakis, N. (2005). Analysis of polycyclic aromatic hydrocarbons in wastewater treatment plant effluents using hollow fibre liquid-phase microextraction. *Chemosphere, 60*(5), 690-698.

Chen, L., Zhang, G., Ge, J., Jiang, P., Liu, Y., & Ran, Y. (2014). Property evaluation of a new selective water shutoff agent for horizontal well. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 446*, 33-45.

Chen, Z., Zhao, L., & Lee, K. (2010). Environmental risk assessment of offshore produced water discharges using a hybrid fuzzy-stochastic modeling approach. *Environmental Modelling & Software, 25*(6), 782-792.

Cheng, L., Bi, X., & Ni, Y. (2011). Oilfield produced water treatment by ozone-enhanced flocculation. Conference proceedings, Computer Distributed Control and Intelligent Environmental Monitoring (CDCIEM), 2011 International Conference on.

Choi, M. (1990). Hydrocyclone produced water treatment for offshore developments. Conference proceedings, SPE Annual Technical Conference and Exhibition.

Choi, Y.-I., & Hong, A. (2007). Ozonation of polycyclic aromatic hydrocarbon in hexane and water: identification of intermediates and pathway. *Korean Journal of Chemical Engineering, 24*(6), 1003-1008.

Chou, C.C., & Hee, S.S.Q. (1992). Microtox EC 50 values for drinking water by-products produced by ozonolysis. *Ecotoxicology and environmental safety, 23*(3), 355-363.

Chu, S., & Majumdar, A. (2012). Opportunities and challenges for a sustainable energy future. *Nature, 488*(7411), 294-303.

Chu, W., & Ma, C.-W. (2000). Quantitative prediction of direct and indirect dye ozonation kinetics. *Water Res, 34*(12), 3153-3160.

Clark, C.E., & Veil, J.A. (2009). Produced Water Volumes and Management Practices in the United States.

Clarke, A., & Harris, C.M. (2003). Polar marine ecosystems: major threats and future change. *Environmental Conservation, 30*(01), 1-25.

Clarke, D., & Ackley, S. (1984). Sea ice structure and biological activity in the Antarctic marginal ice zone. *Journal of Geophysical Research: Oceans, 89*(C2), 2087-2095.

Collins, A. (1975). *Geochemistry of oilfield waters* (Vol. 1): Elsevier.

Corrêa, A.X., Tiepo, E.N., Somensi, C.A., Sperb, R.M., & Radetski, C.M. (2009). Use of ozone-photocatalytic oxidation (O 3/UV/TiO 2) and biological remediation for treatment of produced water from petroleum refineries. *Journal of Environmental Engineering, 136*(1), 40-45.

Cottrell, B.A., Timko, S.A., Devera, L., Robinson, A.K., Gonsior, M., Vizenor, A.E., Simpson, A.J., & Cooper, W.J. (2013). Photochemistry of excited-state species in

natural waters: A role for particulate organic matter. *Water Res, 47*(14), 5189-5199.

Davidson, D.J., Andrews, J., & Pauly, D. (2014). The effort factor: Evaluating the increasing marginal impact of resource extraction over time. *Global Environmental Change, 25*, 63-68.

De Castro, M.L., & Priego-Capote, F. (2007). Ultrasound-assisted preparation of liquid samples. *Talanta, 72*(2), 321-334.

Delgado, B., Pino, V., Ayala, J.H., González, V., & Afonso, A.M. (2004). Nonionic surfactant mixtures: a new cloud-point extraction approach for the determination of PAHs in seawater using HPLC with fluorimetric detection. *Analytica Chimica Acta, 518*(1-2), 165-172.

Deng, S., Yu, G., Jiang, Z., Zhang, R., & Ting, Y.P. (2005). Destabilization of oil droplets in produced water from ASP flooding. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 252*(2), 113-119.

Dietz, C., Sanz, J., & Cámara, C. (2006). Recent developments in solid-phase microextraction coatings and related techniques. *Journal of Chromatography A, 1103*(2), 183-192.

Directorate, N.P. (2011). Facts-The Norwegian Petroleum Sector.

Dong, L., Xiaojun, Z., & Hai'an, Z. (2011). Experimental Study on Inlet Structure of the Rod Pump with Down-Hole Oil-Water Hydrocyclone. *Procedia Engineering, 18*, 369-374.

Donthuan, J., Yunchalard, S., & Srijaranai, S. (2014). Ultrasound-assisted dispersive liquid–liquid microextraction combined with high performance liquid

chromatography for sensitive determination of five biogenic amines in fermented fish samples. *Analytical Methods, 6*(4), 1128.

Dórea, H.S., Bispo, J.R.L., Aragão, K.A.S., Cunha, B.B., Navickiene, S., Alves, J.P.H., Romão, L.P.C., & Garcia, C.A.B. (2007). Analysis of BTEX, PAHs and metals in the oilfield produced water in the State of Sergipe, Brazil. *Microchemical Journal, 85*(2), 234-238.

Dos Santos, E.V., Bezerra Rocha, J.H., De Araujo, D.M., De Moura, D.C., & Martinez-Huitle, C.A. (2014). Decontamination of produced water containing petroleum hydrocarbons by electrochemical methods: a minireview. *Environ Sci Pollut Res Int, 21*(14), 8432-8441.

Durell, G., Røe Utvik, T., Johnsen, S., Frost, T., & Neff, J. (2006). Oil well produced water discharges to the North Sea. Part I: Comparison of deployed mussels (Mytilus edulis), semi-permeable membrane devices, and the DREAM model predictions to estimate the dispersion of polycyclic aromatic hydrocarbons. *Mar Environ Res, 62*(3), 194-223.

Ebrahimi, M., Willershausen, D., Ashaghi, K.S., Engel, L., Placido, L., Mund, P., Bolduan, P., & Czermak, P. (2010). Investigations on the use of different ceramic membranes for efficient oil-field produced water treatment. *Desalination, 250*(3), 991-996.

Echeveste, P., Agustí, S., & Dachs, J. (2011). Cell size dependence of additive versus synergetic effects of UV radiation and PAHs on oceanic phytoplankton. *Environmental Pollution, 159*(5), 1307-1316.

Ekins, P., Vanner, R., & Firebrace, J. (2005). Management of produced water on offshore oil installations: a comparative assessment using flow analysis.

Ekins, P., Vanner, R., & Firebrace, J. (2007). Zero emissions of oil in water from offshore oil and gas installations: economic and environmental implications. *Journal of Cleaner Production, 15*(13–14), 1302-1315.

Elias - Samlalsingh, N., & Agard, J.B. (2004). Application of toxicity identification evaluation procedures for characterizing produced water using the tropical mysid, Metamysidopsis insularis. *Environmental Toxicology and Chemistry, 23*(5), 1194-1203.

Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L.C., Biak, D.R., Madaeni, S.S., & Abidin, Z.Z. (2009). Review of technologies for oil and gas produced water treatment. *J Hazard Mater, 170*(2-3), 530-551.

Fakhru'l-Razi, A., Pendashteh, A., Abidin, Z.Z., Abdullah, L.C., Biak, D.R.A., & Madaeni, S.S. (2010). Application of membrane-coupled sequencing batch reactor for oilfield produced water recycle and beneficial re-use. *Bioresource Technology, 101*(18), 6942-6949.

Faksness, L.-G., Grini, P.G., & Daling, P.S. (2004). Partitioning of semi-soluble organic compounds between the water phase and oil droplets in produced water. *Mar Pollut Bull, 48*(7), 731-742.

Fasnacht, M.P., & Blough, N.V. (2002). Aqueous photodegradation of polycyclic aromatic hydrocarbons. *Environ Sci Technol, 36*(20), 4364-4369.

Fasnacht, M.P., & Blough, N.V. (2003). Kinetic analysis of the photodegradation of polycyclic aromatic hydrocarbons in aqueous solution. *Aquatic Sciences - Research Across Boundaries, 65*(4), 352-358.

Fraser, G.S. (2014). Impacts of Offshore Oil and Gas Development on Marine Wildlife Resources. In J. E. Gates, D. L. Trauger & B. Czech (Eds.), *Peak Oil, Economic Growth, and Wildlife Conservation* (pp. 191-217). New York, NY: Springer New York.

Frid, C.L. (2003). Bioaccumulation in Marine Organisms. Effect of Contaminants from Oil Well Produced Water. *Organic Geochemistry, 34*(1).

Gautier, D.L., Bird, K.J., Charpentier, R.R., Grantz, A., Houseknecht, D.W., Klett, T.R., Moore, T.E., Pitman, J.K., *et al.* (2009). Assessment of Undiscovered Oil and Gas in the Arctic. *Science, 324*(5931), 1175.

Gioti, E.M., Skalkos, D.C., Fiamegos, Y.C., & Stalikas, C.D. (2005). Single-drop liquid-phase microextraction for the determination of hypericin, pseudohypericin and hyperforin in biological fluids by high performance liquid chromatography. *Journal of Chromatography A, 1093*(1), 1-10.

Gupta, S., Pathak, B., & Fulekar, M. (2015). Molecular approaches for biodegradation of polycyclic aromatic hydrocarbon compounds: a review. *Reviews in Environmental Science and Bio/Technology, 14*(2), 241-269.

Haapea, P., & Tuhkanen, T. (2006). Integrated treatment of PAH contaminated soil by soil washing, ozonation and biological treatment. *J Hazard Mater, 136*(2), 244-250.

Hamilton, J.M. (2011). The Challenges of Deep Water Arctic Development. Conference proceedings, The Twenty-first International Offshore and Polar Engineering Conference.

Hamlat, M., Djeffal, S., & Kadi, H. (2001). Assessment of radiation exposures from naturally occurring radioactive materials in the oil and gas industry. *Applied Radiation and Isotopes, 55*(1), 141-146.

Hansen, B., & Davies, S. (1994). Review of potential technologies for the removal of dissolved components from produced water. *Chemical engineering research & design, 72*(2), 176-188.

Haritash, A., & Kaushik, C. (2009). Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. *J Hazard Mater, 169*(1), 1-15.

Harsem, Ø., Eide, A., & Heen, K. (2011). Factors influencing future oil and gas prospects in the Arctic. *Energy Policy, 39*(12), 8037-8045.

Hatch, A., & Burton, G. (1999). Photo-induced toxicity of PAHs to Hyalella azteca and Chironomus tentans: effects of mixtures and behavior. *Environmental Pollution, 106*(2), 157-167.

Hawboldt, K., Chen, B., Thanyamanta, W., Egli, S., & Gryshchenko, A. (2010). Review of produced water management and challenges in harsh/arctic environments. *Submitted to the American Bureau of Shipping (ABS).*

Hayes, T., & Arthur, D. (2004). Overview of emerging produced water treatment technologies. Conference proceedings, 11th Annual International Petroleum Environmental Conference, Albuquerque, NM.

HELCOM. (2007). HELCOM Baltic Sea Action Plan, Environment.

Henderson, S.B., Grigson, S.J.W., Johnson, P., & Roddie, B.D. (1999). Potential Impact of Production Chemicals on the Toxicity of Produced Water Discharges from North Sea Oil Platforms. *Mar Pollut Bull, 38*(12), 1141-1151.

Henner, P., Schiavon, M., Morel, J.-L., & Lichtfouse, E. (1997). Polycyclic aromatic hydrocarbon (PAH) occurrence and remediation methods. *Analusis, 25*(9-10), M56-M59.

Hillie, T., & Hlophe, M. (2007). Nanotechnology and the challenge of clean water. *Nature Nanotechnology, 2*(11), 663-664.

Holdway, D.A. (2002). The acute and chronic effects of wastes associated with offshore oil and gas production on temperate and tropical marine ecological processes. *Mar Pollut Bull, 44*(3), 185-203.

Hollender, J., Zimmermann, S.G., Koepke, S., Krauss, M., McArdell, C.S., Ort, C., Singer, H., von Gunten, U., *et al.* (2009). Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a full-scale post-ozonation followed by sand filtration. *Environ Sci Technol, 43*(20), 7862-7869.

Hong, P.A., & Xiao, T. (2013). Treatment of oil spill water by ozonation and sand filtration. *Chemosphere, 91*(5), 641-647.

Hou, L., & Lee, H.K. (2004). Determination of pesticides in soil by liquid-phase microextraction and gas chromatography–mass spectrometry. *Journal of Chromatography A, 1038*(1), 37-42.

Huang, W.-J., Chang, C.-Y., & Shih, F.-H. (2009). Disinfection by-product formation and mutagenic assay caused by preozonation of groundwater containing bromide. *Environmental monitoring and assessment, 158*(1-4), 181-196.

Igunnu, E.T., & Chen, G.Z. (2012). Produced water treatment technologies. *International Journal of Low-Carbon Technologies*, cts049.

Igunnu, E.T., & Chen, G.Z. (2014). Produced water treatment technologies. *International Journal of Low-Carbon Technologies, 9*(3), 157-177.

Ikehata, K., & El-Din, M.G. (2004). Degradation of recalcitrant surfactants in wastewater by ozonation and advanced oxidation processes: a review. *Ozone: Science & Engineering, 26*(4), 327-343.

Ikehata, K., & Gamal El-Din, M. (2005a). Aqueous Pesticide Degradation by Ozonation and Ozone-Based Advanced Oxidation Processes: A Review (Part II). *Ozone: Science & Engineering, 27*(3), 173-202.

Ikehata, K., & Gamal El-Din, M. (2005b). Aqueous pesticide degradation by ozonation and ozone-based advanced oxidation processes: a review (Part I). *Ozone: Science and Engineering, 27*(2), 83-114.

Ikehata, K., Jodeiri Naghashkar, N., & Gamal El-Din, M. (2006). Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: a review. *Ozone: Science and Engineering, 28*(6), 353-414.

Ikehata, K., Gamal El-Din, M., & Snyder, S.A. (2008). Ozonation and advanced oxidation treatment of emerging organic pollutants in water and wastewater. *Ozone: Science and Engineering, 30*(1), 21-26.

Inc., B.E. (2012). Oil discharge prevention and contingency plan.

Jacobs, L.E., Weavers, L.K., & Chin, Y.-P. (2008). Direct and indirect photolysis of polycyclic aromatic hydrocarbons in nitrate-rich surface waters. *Environmental Toxicology and Chemistry, 27*(8), 1643-1648.

Jasper, J.T., & Sedlak, D.L. (2013). Phototransformation of wastewater-derived trace organic contaminants in open-water unit process treatment wetlands. *Environ Sci Technol, 47*(19), 10781-10790.

Javier Benitez, F., Acero, J.L., Real, F.J., & Maya, C. (2004). Modeling of photooxidation of acetamide herbicides in natural waters by UV radiation and the combinations UV/H2O2 and UV/O3. *Journal of Chemical Technology & Biotechnology, 79*(9), 987-997.

Ji, G.D., Sun, T.H., & Ni, J.R. (2007). Surface flow constructed wetland for heavy oil-produced water treatment. *Bioresource Technology, 98*(2), 436-441.

Jing, L., Chen, B., Zhang, B., & Peng, H. (2012). A review of ballast water management practices and challenges in harsh and arctic environments. *Environmental Reviews, 20*(2), 83-108.

Jing, L., Chen, B., & Zhang, B. (2014a). Modeling of UV-Induced Photodegradation of Naphthalene in Marine Oily Wastewater by Artificial Neural Networks. *Water, Air, & Soil Pollution, 225*(4).

Jing, L., Chen, B., Zhang, B., Zheng, J., & Liu, B. (2014b). Naphthalene degradation in seawater by UV irradiation: the effects of fluence rate, salinity, temperature and initial concentration. *Mar Pollut Bull, 81*(1), 149-156.

Jing, L., Chen, B., Zhang, B., & Li, P. (2015). Process simulation and dynamic control for marine oily wastewater treatment using UV irradiation. *Water Res, 81*, 101-112.

Jiuhui, Q. (2008). Research progress of novel adsorption processes in water purification: A review. *Journal of Environmental Sciences, 20*(1), 1-13.

Johnsen, S., Røe Utvik, T.I., Garland, E., de Vals, B., & Campbell, J. (2004). Environmental fate and effect of contaminants in produced water. Conference proceedings, SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production.

Kahan, T.F., Zhao, R., Jumaa, K.B., & Donaldson, D.J. (2010). Anthracene Photolysis in Aqueous Solution and Ice: Photon Flux Dependence and Comparison of Kinetics in Bulk Ice and at the Air−Ice Interface. *Environ Sci Technol, 44*(4), 1302-1306.

Kalmar, J., Doka, E., Lente, G., & Fabian, I. (2014). Aqueous photochemical reactions of chloride, bromide, and iodide ions in a diode-array spectrophotometer. Autoinhibition in the photolysis of iodide ions. *Dalton Trans, 43*(12), 4862-4870.

Kazemimoghadam, M. (2010). New nanopore zeolite membranes for water treatment. *Desalination, 251*(1), 176-180.

Kelly, B.C., & Gobas, F.A. (2003). An arctic terrestrial food-chain bioaccumulation model for persistent organic pollutants. *Environ Sci Technol, 37*(13), 2966-2974.

Khan, F., Ahmed, S., Yang, M., Hashemi, S.J., Caines, S., Rathnayaka, S., & Oldford, D. (2015). Safety challenges in harsh environments: Lessons learned. *Process Safety Progress, 34*(2), 191-195.

Khatib, Z., & Verbeek, P. (2002). *Water to Value - Produced Water Management for Sustainable Field Development of Mature and Green Fields*. Paper presented at the SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Kuala Lumpur, Malaysia.

King, A.J., Readman, J.W., & Zhou, J.L. (2004). Determination of polycyclic aromatic hydrocarbons in water by solid-phase microextraction–gas chromatography–mass spectrometry. *Analytica Chimica Acta, 523*(2), 259-267.

Kishimoto, N., & Nakamura, E. (2011). Effects of ozone-gas bubble size and pH on ozone/UV treatment. *Ozone: Science & Engineering, 33*(5), 396-402.

Klamerth, N., Moreira, J., Li, C., Singh, A., McPhedran, K.N., Chelme-Ayala, P., Belosevic, M., & El-Din, M.G. (2015). Effect of ozonation on the naphthenic acids' speciation and toxicity of pH-dependent organic extracts of oil sands process-affected water. *Science of the total environment, 506*, 66-75.

Klasson, K.T., Tsouris, C., Jones, S.A., Dinsmore, M.D., Walker, A.B., DePaoli, D.W., Yiacoumi, S., Vithayaveroj, V., *et al.* (2002). Ozone treatment of soluble organics in produced water. Conference proceedings, Petroleum Environmental Research Forum Project.

Knol, M. (2011). The uncertainties of precaution: Zero discharges in the Barents Sea. *Marine Policy, 35*(3), 399-404.

Köhler, A., Hellweg, S., Escher, B.I., & Hungerbühler, K. (2006). Organic pollutant removal versus toxicity reduction in industrial wastewater treatment: The example of wastewater from fluorescent whitening agent production. *Environ Sci Technol, 40*(10), 3395-3401.

Kornmüller, A., & Wiesmann, U. (2003). Ozonation of polycyclic aromatic hydrocarbons in oil/water-emulsions: mass transfer and reaction kinetics. *Water Res, 37*(5), 1023-1032.

Krause, P.R. (1995). Spatial and temporal variability in receiving water toxicity near an oil effluent discharge site. *Archives of Environmental Contamination and Toxicology, 29*(4), 523-529.

Krebs, T., Schroën, C., & Boom, R. (2013). Coalescence kinetics of oil-in-water emulsions studied with microfluidics. *Fuel, 106*, 327-334.

Ku, Y.C., Leong, M.I., Wang, W.T., & Huang, S.D. (2013). Up‐and‐down shaker‐assisted ionic liquid‐based dispersive liquid—liquid microextraction of benzophenone‐type ultraviolet filters. *J Sep Sci, 36*(8), 1470-1477.

Kwon, S.H., Kim, J.H., & Cho, D. (2009). An analysis method for degradation kinetics of lowly concentrated PAH solutions under UV light and ultrasonication. *Journal of Industrial and Engineering Chemistry, 15*(2), 157-162.

Ledakowicz, S., Miller, J.S., & Olejnik, D. (2001). Oxidation of PAHs in water solution by ozone combined with ultraviolet radiation. *International Journal of Photoenergy, 3*(2), 95-101.

Lee, K., Cobanli, S.E., Robinson, B.J., & Wohlgeschaffen, G. (2011). Application of microbiological methods to assess the potential impact of produced water discharges *Produced Water* (pp. 353-373): Springer.

Lehto, K.-M., Vuorimaa, E., & Lemmetyinen, H. (2000). Photolysis of polycyclic aromatic hydrocarbons (PAHs) in dilute aqueous solutions detected by fluorescence. *Journal of Photochemistry and Photobiology A: Chemistry, 136*(1–2), 53-60.

Li, Y.S., Yan, L., Xiang, C.B., & Hong, L.J. (2006). Treatment of oily wastewater by organic–inorganic composite tubular ultrafiltration (UF) membranes. *Desalination, 196*(1), 76-83.

Liangxiong, L., Whitworth, T., & Lee, R. (2003). Separation of inorganic solutes from oil-field produced water using a compacted bentonite membrane. *Journal of Membrane Science, 217*(1), 215-225.

Lin, C., Zhang, W., Yuan, M., Feng, C., Ren, Y., & Wei, C. (2014). Degradation of polycyclic aromatic hydrocarbons in a coking wastewater treatment plant residual by an O3/ultraviolet fluidized bed reactor. *Environmental Science and Pollution Research, 21*(17), 10329-10338.

Liu, B., Chen, B., Lee, K., Zhang, B., Ma, Y., & Jing, L. (2014). Photocatalytic degradation of naphthalene in offshore produced water: comparison of immobilized and suspended TiO2. Conference proceedings, The International Conference on Marine and Freshwater Environments (iMFE 2014).

Liu, N., Li, L., McPherson, B., & Lee, R. (2008). Removal of organics from produced water by reverse osmosis using MFI-type zeolite membranes. *Journal of Membrane Science, 325*(1), 357-361.

Liu, S., Zhang, Z., Dong, X., Zhao, X., & Du, W. (2005). Treatment of ASP produced water with hydrophilic fibre ball filtration. Conference proceedings, The Fifteenth International Offshore and Polar Engineering Conference.

Lourenço, R.A., Júnior, M.A.A., Júnior, R.O.M., Macena, L.F., Lima, E.F.d.A., & Carneiro, M.E.R. (2013). Aliphatic and polycyclic aromatic hydrocarbons and trace elements as indicators of contamination status near oil and gas platforms in

the Sergipe–Alagoas Basin (Southwest Atlantic Ocean). *Continental Shelf Research, 71*, 37-44.

Lucas, M.S., Peres, J.A., & Puma, G.L. (2010). Treatment of winery wastewater by ozone-based advanced oxidation processes (O 3, O 3/UV and O 3/UV/H 2 O 2) in a pilot-scale bubble column reactor and process economics. *Separation and Purification Technology, 72*(3), 235-241.

Macdonald, R., & Bewers, J. (1996). Contaminants in the arctic marine environment: priorities for protection. *ICES Journal of Marine Science: Journal du Conseil, 53*(3), 537-563.

Macdonald, R.W., Hamer, T., Fyfe, J., Loeng, H., & Weingartner, T. (2003). *AMAP Assessment 2002: The Influence of Global Change on Contaminant Pathways to, within, and from the Arctic*: Arctic Monitoring and Assessment Programme (AMAP).

MAERSK. (2011). 2011. Environmental Status Report 2011-The Danish North Sea.

Mahmoudi, S. (1997). Legal protection of the Persian Gulf's marine environment. *Marine Policy, 21*(1), 53-62.

Manfra, L., Moltedo, G., Lamberti, C.V., Maggi, C., Finoia, M.G., Giuliani, S., Onorati, F., Gabellini, M., *et al.* (2007). Metal Content and Toxicity of Produced Formation Water (PFW): Study of the Possible Effects of the Discharge on Marine Environment. *Archives of Environmental Contamination and Toxicology, 53*(2), 183-190.

Manoli, E., & Samara, C. (1999). Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. *TrAC Trends in Analytical Chemistry, 18*(6), 417-428.

Manoli, E., & Samara, C. (2008). The removal of polycyclic aromatic hydrocarbons in the wastewater treatment process: experimental calculations and model predictions. *Environmental Pollution, 151*(3), 477-485.

Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., De Alencastro, L.F., Abegglen, C., Thonney, D., *et al.* (2013). Treatment of micropollutants in municipal wastewater: ozone or powdered activated carbon? *Science of the total environment, 461*, 480-498.

Martin, J.W., Barri, T., Han, X., Fedorak, P.M., El-Din, M.G., Perez, L., Scott, A.C., & Jiang, J.T. (2010). Ozonation of oil sands process-affected water accelerates microbial bioremediation. *Environ Sci Technol, 44*(21), 8350-8356.

Mastouri, R., & Nadim, F. (2010). 2010: A Time To Review The Produced Water Treatment Technologies, A Time To Look Forward For New Management Policies.

McIntosh, S., King, T., Wu, D., & Hodson, P.V. (2010). Toxicity of dispersed weathered crude oil to early life stages of Atlantic herring (Clupea harengus). *Environmental Toxicology and Chemistry, 29*(5), 1160-1167.

Menor‐Salván, C., Ruiz-Bermejo, M., Osuna-Esteban, S., Mu?oz-Caro, G., & Veintemillas-Verdaguer, S. (2008). Synthesis of Polycyclic Aromatic

Hydrocarbons and Acetylene Polymers in Ice: A Prebiotic Scenario. *Chemistry & Biodiversity, 5*(12), 2729-2739.

Michałowicz, J., & Duda, W. (2007). Phenols – Sources and Toxicity. *Polish J. of Environ. Stud., 16*(3), 347-362.

Middleditch, B.S. (1984). Ecological effects of produced water effluents from offshore oil and gas production platforms. *Ocean management, 9*(3-4), 191-316.

Miller, J.S., & Olejnik, D. (2001). Photolysis of polycyclic aromatic hydrocarbons in water. *Water Res, 35*(1), 233-243.

Mitchell, R.K., & Salvo, G.S. (1990). A procedure to shut off high-pressure water flows during primary cementing. *SPE Drilling Engineering, 5*(03), 191-195.

Mondal, S., & Wickramasinghe, S.R. (2008). Produced water treatment by nanofiltration and reverse osmosis membranes. *Journal of Membrane Science, 322*(1), 162-170.

Moosai, R., & Dawe, R.A. (2003). Gas attachment of oil droplets for gas flotation for oily wastewater cleanup. *Separation and Purification Technology, 33*(3), 303-314.

Morrow, L.R., Martir, W.K., Aghazeynali, H., & Wright, D.E. (1999). Process of treating produced water with ozone: Google Patents.

Multon, L., & Viraraghavan, T. (2006). Removal of oil from produced water by coalescence/filtration in a granular bed. *Environmental Technology, 27*(5), 529-544.

Naddeo, V., Rizzo, L., & Belgiorno, V. (2011). *Water, wastewater and soil treatment by advanced oxidation processes*: Edizioni ASTER.

Nasr-El-Din, H., & Taylor, K. (2005). Evaluation of sodium silicate/urea gels used for water shut-off treatments. *Journal of Petroleum Science and Engineering, 48*(3), 141-160.

NEB, C-NLOPB, & CNSOPB. (2010). Offshore Waste Treatment Guidelines.

Neff, J., Lee, K., & DeBlois, E.M. (2011). Produced Water: Overview of Composition, Fates, and Effects. In K. Lee & J. Neff (Eds.), *Produced Water: Environmental Risks and Advances in Mitigation Technologies* (pp. 3-54). New York, NY: Springer New York.

Neff, J.M. (2002). *Bioaccumulation in marine organisms: effect of contaminants from oil well produced water*: Elsevier.

Neff, J.M., Johnsen, S., Frost, T.K., Røe Utvik, T.I., & Durell, G.S. (2006). Oil well produced water discharges to the North Sea. Part II: Comparison of deployed mussels (Mytilus edulis) and the DREAM model to predict ecological risk. *Mar Environ Res, 62*(3), 224-246.

NETL. (2010). Produced Water Management Information System.

NETL. (2013). Oil & Natrual Gas Program Newsletter.

Noble, B., Ketilson, S., Aitken, A., & Poelzer, G. (2013). Strategic environmental assessment opportunities and risks for Arctic offshore energy planning and development. *Marine Policy, 39*, 296-302.

O'Hara, P.D., & Morandin, L.A. (2010). Effects of sheens associated with offshore oil and gas development on the feather microstructure of pelagic seabirds. *Mar Pollut Bull, 60*(5), 672-678.

Oneby, M.A., Bromley, C.O., Borchardt, J.H., & Harrison, D.S. (2010). Ozone treatment of secondary effluent at US municipal wastewater treatment plants. *Ozone: Science & Engineering, 32*(1), 43-55.

Oppenländer, T. (2003). *Photochemical Purification of Water and Air: Advanced Oxidation Processes (AOPs)-Principles, Reaction Mechanisms, Reactor Concepts*: John Wiley & Sons.

Orem, W.H., Tatu, C.A., Lerch, H.E., Rice, C.A., Bartos, T.T., Bates, A.L., Tewalt, S., & Corum, M.D. (2007). Organic compounds in produced waters from coalbed natural gas wells in the Powder River Basin, Wyoming, USA. *Applied Geochemistry, 22*(10), 2240-2256.

OSPAR. (2013). Background Document concerning Techniques for the Management of Produced Water from Offshore Installations.

Otton, J.K. (2006). Environmental Aspects of Produced-water Salt Releases in Onshore and Coastal Petroleum-producing Areas of the Conterminous U.S. – A Bibliography: USGS.

Ozcan, S., Tor, A., & Aydin, M.E. (2010). Determination of polycyclic aromatic hydrocarbons in waters by ultrasound-assisted emulsification-microextraction and gas chromatography-mass spectrometry. *Anal Chim Acta, 665*(2), 193-199.

Pavasovic, A. (1996). The Mediterranean Action Plan phase II and the revised Barcelona Convention: new prospective for integrated coastal management in the Mediterranean region. *Ocean & Coastal Management, 31*(2), 133-182.

Pereira, A.S., Islam, M., Gamal El‐Din, M., & Martin, J.W. (2013). Ozonation degrades all detectable organic compound classes in oil sands process‐affected water; an application of high‐performance liquid chromatography/obitrap mass spectrometry. *Rapid Communications in Mass Spectrometry, 27*(21), 2317-2326.

Pérez-Casanova, J.C., Hamoutene, D., Samuelson, S., Burt, K., King, T.L., & Lee, K. (2010). The immune response of juvenile Atlantic cod (Gadus morhua L.) to chronic exposure to produced water. *Mar Environ Res, 70*(1), 26-34.

Perraudin, E., Budzinski, H., & Villenave, E. (2007a). Identification and quantification of ozonation products of anthracene and phenanthrene adsorbed on silica particles. *Atmospheric Environment, 41*(28), 6005-6017.

Perraudin, E., Budzinski, H., & Villenave, E. (2007b). Kinetic study of the reactions of ozone with polycyclic aromatic hydrocarbons adsorbed on atmospheric model particles. *Journal of Atmospheric Chemistry, 56*(1), 57-82.

Pfirman, S., Eicken, H., Bauch, D., & Weeks, W. (1995). The potential transport of pollutants by Arctic sea ice. *Science of the total environment, 159*(2), 129-146.

Pino, V., Ayala, J.H., Afonso, A.M., & González, V. (2002). Determination of polycyclic aromatic hydrocarbons in seawater by high-performance liquid chromatography with fluorescence detection following micelle-mediated preconcentration. *Journal of Chromatography A, 949*(1–2), 291-299.

Pinturier, L.M., Moltu, U.E., Buffagni, M., & Bracco, L. (2008). Environmental Risk Management in the Barents Sea: Contribution to scientific based approach for defining acceptance criteria for operational activity in the Barents Sea. Conference

proceedings, SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production.

Popp, P., Bauer, C., & Wennrich, L. (2001). Application of stir bar sorptive extraction in combination with column liquid chromatography for the determination of polycyclic aromatic hydrocarbons in water samples. *Analytica Chimica Acta, 436*(1), 1-9.

Poznyak, T., & Vivero, J. (2005). Degradation of aqueous phenol and chlorinated phenols by ozone. *Ozone: Science and Engineering, 27*(6), 447-458.

Psillakis, E., Mantzavinos, D., & Kalogerakis, N. (2004). Monitoring the sonochemical degradation of phthalate esters in water using solid-phase microextraction. *Chemosphere, 54*(7), 849-857.

Qing, Y., Yefei, W., Wei, Z., Ziyuan, Q., & Fulin, Z. (2009). Study and application of gelled foam for in-depth water shutoff in a fractured oil reservoir. *Journal of Canadian Petroleum Technology, 48*(12), 51-55.

Rakness, K.L. (2011). *Ozone in drinking water treatment: process design, operation, and optimization*: American Water Works Association.

Ranck, J., Bowman, R., Weeber, J., Katz, L., & Sullivan, E. (2005). BTEX Removal from Produced Water Using Surfactant-Modified Zeolite. *Journal of Environmental Engineering, 131*(3), 434-442.

Reynolds, J., & Tenhunen, J. (1996). Ecosystem response, resistance, resilience, and recovery in Arctic landscapes: Introduction *Landscape function and disturbance in arctic tundra* (pp. 3-18): Springer.

Rhee, C.H., Martyn, P.C., & Kremer, J. (1989). Removal of oil and grease in oil processing wastewater. *Sanitation District of Los Angeles County, USA*.

Robinson, D. (2013). Oil and gas: Treatment and discharge of produced waters onshore. *Filtration+ Separation, 50*(3), 40-46.

Romero, M.T., & Ferrer, N. (1999). Determination of oil and grease by solid phase extraction and infrared spectroscopy. *Analytica Chimica Acta, 395*(1), 77-84.

Rubio-Clemente, A., Torres-Palma, R.A., & Peñuela, G.A. (2014). Removal of polycyclic aromatic hydrocarbons in aqueous environment by chemical treatments: a review. *Science of the total environment, 478*, 201-225.

Rubio, J., Souza, M., & Smith, R. (2002). Overview of flotation as a wastewater treatment technique. *Minerals engineering, 15*(3), 139-155.

Russo, L., Rizzo, L., & Belgiorno, V. (2010). PAHs contaminated soils remediation by ozone oxidation. *Desalination and Water Treatment, 23*(1-3), 161-172.

Rye, S., & Marcussen, E. (1993). A new method for removal of oil in produced water. Conference proceedings, Offshore Europe.

Sadarta, B., Caie, D., & Adimartapraja, N. (2000). Field Case of Water Shut-Off with Crosslinked Polymer in Handil Field, Kalimantan, Indonesia.

Sanchez-Prado, L., Barro, R., Garcia-Jares, C., Llompart, M., Lores, M., Petrakis, C., Kalogerakis, N., Mantzavinos, D., *et al.* (2008). Sonochemical degradation of triclosan in water and wastewater. *Ultrasonics Sonochemistry, 15*(5), 689-694.

Santiago-Morales, J., Gómez, M.J., Herrera-López, S., Fernández-Alba, A.R., García-Calvo, E., & Rosal, R. (2013). Energy efficiency for the removal of non-polar

pollutants during ultraviolet irradiation, visible light photocatalysis and ozonation of a wastewater effluent. *Water Res, 47*(15), 5546-5556.

Sarafraz-Yazdi, A., & Amiri, A. (2010). Liquid-phase microextraction. *TrAC Trends in Analytical Chemistry, 29*(1), 1-14.

Saraji, M., & Boroujeni, M.K. (2014). Recent developments in dispersive liquid-liquid microextraction. *Anal Bioanal Chem, 406*(8), 2027-2066.

Schwarz, F.P., & Wasik, S.P. (1976). Fluorescence measurements of benzene, naphthalene, anthracene, pyrene, fluoranthene, and benzo [e] pyrene in water. *Analytical chemistry, 48*(3), 524-528.

Scurlock, R., Rougee, M., & Bensasson, R.V. (1990). Redox properties of phenols, their relationships to singlet oxygen quenching and to their inhibitory effects on benzo (a) pyrene-induced neoplasia. *Free radical research communications, 8*(4-6), 251-258.

Seright, R., Lane, R., & Sydansk, R. (2001). A strategy for attacking excess water production. Conference proceedings, SPE Permian Basin Oil and Gas Recovery Conference.

Shaffer, D.L., Arias Chavez, L.H., Ben-Sasson, M., Romero-Vargas Castrillón, S., Yip, N.Y., & Elimelech, M. (2013). Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions. *Environ Sci Technol, 47*(17), 9569-9583.

Shafian, M., Rohaida, S., Hassan, A., Bin, A., Ismail, S., Teng, L.K., & Irawan, S. (2010). Blocked Isocyanate Fluid System for Water Shut off Application. Conference

proceedings, IADC/SPE Asia Pacific Drilling Technology Conference and Exhibition.

Sharqawy, M.H., Lienhard V, J.H., & Zubair, S.M. (2011). Erratum to Thermophysical properties of seawater: a review of existing correlations and data. *Desalination and Water Treatment, 29*(1-3), 355-355.

Shemer, H., & Linden, K.G. (2007). Photolysis, oxidation and subsequent toxicity of a mixture of polycyclic aromatic hydrocarbons in natural waters. *J Photochem Photobiol A Chem, 187*(2-3), 186-195.

Shiu, W.Y., Bobra, M., Bobra, A.M., Maijanen, A., Suntio, L., & Mackay, D. (1990). The water solubility of crude oils and petroleum products. *Oil and Chemical pollution, 7*(1), 57-84.

Shpiner, R., Liu, G., & Stuckey, D.C. (2009). Treatment of oilfield produced water by waste stabilization ponds: Biodegradation of petroleum-derived materials. *Bioresource Technology, 100*(24), 6229-6235.

Simjoo, M., Koohi, A.D., Seftie, M.V., & Zitha, P.L.J. (2009). Water shut-off in a fractured system using a robust polymer gel. Conference proceedings, 8th European Formation Damage Conference.

Sirivedhin, T., & Dallbauman, L. (2004). Organic matrix in produced water from the Osage-Skiatook petroleum environmental research site, Osage county, Oklahoma. *Chemosphere, 57*(6), 463-469.

Smit, D., Mathijs, G., Frost, T.K., & Johnsen, S. (2011). Achievements of risk‐based produced water management on the Norwegian continental shelf (2002–2008). *Integrated environmental assessment and management, 7*(4), 668-677.

Somerville, H., Bennett, D., Davenport, J., Holt, M., Lynes, A., Mahieu, A., McCourt, B., Parker, J., *et al.* (1987). Environmental effect of produced water from North Sea oil operations. *Mar Pollut Bull, 18*(10), 549-558.

Song, X., Li, J., Liao, C., & Chen, L. (2011). Ultrasound-Assisted Dispersive Liquid–Liquid Microextraction Combined with Low Solvent Consumption for Determination of Polycyclic Aromatic Hydrocarbons in Seawater by GC–MS. *Chromatographia, 74*(1-2), 89-98.

Souza Duarte, J.P., Martínez-HuitIe, C.A., & da SiIva, D.R. (2011). Electrochemical treatment for removing petroleum polycyclic aromatic hydrocarbons (PAHs) from synthetic produced water using a DSA-type anode: Preliminary results. *Sustainable Environment Research, 21*(5).

Souza, J., Paiva, M., Farias, F., Neto, S.F., & Lima, A. (2012). Hydrocyclone Applications in Produced Water: A Steady-State Numerical Analysis. *Brazilian Journal of Petroleum and Gas, 6*(3).

Spielhagen, R.F., Baumann, K.-H., Erlenkeuser, H., Nowaczyk, N.R., Nørgaard-Pedersen, N., Vogt, C., & Weiel, D. (2004). Arctic Ocean deep-sea record of northern Eurasian ice sheet history. *Quaternary Science Reviews, 23*(11), 1455-1483.

Stagg, R.M., & McIntosh, A. (1996). Hydrocarbon concentrations in the northern North Sea and effects on fish larvae. *Science of the total environment, 186*(3), 189-201.

Stalter, D., Magdeburg, A., Wagner, M., & Oehlmann, J. (2011). Ozonation and activated carbon treatment of sewage effluents: Removal of endocrine activity and cytotoxicity. *Water Res, 45*(3), 1015-1024.

Stasinakis, A. (2008). Use of selected advanced oxidation processes (AOPs) for wastewater treatment—a mini review. *Global NEST journal, 10*(3), 376-385.

Stephenson, M. (1992a). Components of produced water: a compilation of industry studies. *Journal of Petroleum Technology, 44*(05), 548-603.

Stephenson, M. (1992b). A Survey of Produced Water Studies. In J. P. Ray & F. R. Engelhardt (Eds.), *Produced Water: Technological/Environmental Issues and Solutions* (pp. 1-11). Boston, MA: Springer US.

Stepnowski, P., Siedlecka, E., Behrend, P., & Jastorff, B. (2002). Enhanced photo-degradation of contaminants in petroleum refinery wastewater. *Water Res, 36*(9), 2167-2172.

Szép, A., & Kohlheb, R. (2010). Water treatment technology for produced water. *Water Science and Technology, 62*(10), 2372-2380.

Tehrani-Bagha, A.R., Nikkar, H., Menger, F., & Holmberg, K. (2012). Degradation of two persistent surfactants by UV-enhanced ozonation. *Journal of Surfactants and Detergents, 15*(1), 59-66.

Thanasukarn, P., Pongsawatmanit, R., & McClements, D.J. (2006). Utilization of layer-by-layer interfacial deposition technique to improve freeze–thaw stability of oil-in-water emulsions. *Food research international, 39*(6), 721-729.

Thomson, C., Broadbent, C., & Prest, H. (2007). The 5975C Series MSDs: Guidanc e in implementing high ion source temperatures. *Agilent Technical Note*.

Tibbetts, P.J.C., Buchanan, I.T., Gawel, L.J., & Large, R. (1992). A Comprehensive Determination of Produced Water Composition. In J. P. Ray & F. R. Engelhardt (Eds.), *Produced Water: Technological/Environmental Issues and Solutions* (pp. 97-112). Boston, MA: Springer US.

Titato, G.M., & Lanças, F.M. (2006). Optimization and validation of HPLC-UV-DAD and HPLC-APCI-MS methodologies for the determination of selected PAHs in water samples. *Journal of chromatographic science, 44*(1), 35-40.

Trapido, M., Veressinina, J., & Munter, R. (1994). Ozonation and AOP treatment of phenanthrene in aqueous solutions. *Ozone: Science & Engineering, 16*(6), 475-485.

Tromp, D., & Wieriks, K. (1994). The OSPAR convention: 25 years of North Sea protection. *Mar Pollut Bull, 29*(6-12), 622-626.

Tseng, W.-C., Chen, P.-S., & Huang, S.-D. (2014). Optimization of two different dispersive liquid–liquid microextraction methods followed by gas chromatography–mass spectrometry determination for polycyclic aromatic hydrocarbons (PAHs) analysis in water. *Talanta, 120*, 425-432.

Utvik, T.I.R. (1999). Chemical characterisation of produced water from four offshore oil production platforms in the North Sea. *Chemosphere, 39*(15), 2593-2606.

Van Scoy, A.R., Lin, C.Y., Anderson, B.S., Philips, B.M., Martin, M.J., McCall, J., Todd, C.R., Crane, D., *et al.* (2010). Metabolic responses produced by crude versus

dispersed oil in Chinook salmon pre-smolts via NMR-based metabolomics. *Ecotoxicology and environmental safety, 73*(5), 710-717.

Veil, J., & Clark, C. (2011). Produced Water Volume Estimates and Management Practices. *SPE Production & Operations, 26*(03), 234 - 239.

Veil, J.A., Puder, M.G., Elcock, D., & Redweik, R.J. (2004). A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane.

Vione, D., Calza, P., Galli, F., Fabbri, D., Santoro, V., & Medana, C. (2015). The role of direct photolysis and indirect photochemistry in the environmental fate of ethylhexyl methoxy cinnamate (EHMC) in surface waters. *Sci Total Environ, 537*, 58-68.

Von Gunten, U. (2003a). Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Res, 37*(7), 1443-1467.

Von Gunten, U. (2003b). Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Res, 37*(7), 1469-1487.

Voordouw, G., Agrawal, A., Park, H.-S., Gieg, L.M., Jack, T.R., Cavallaro, A.N., Granli, T., & Miner, K. (2011). Souring treatment with nitrate in fields from which oil is produced by produced water reinjection. Conference proceedings, SPE International Symposium on Oilfield Chemistry.

Walker, A.B., Tsouris, C., DePaoli, D.W., & Thomas Klasson, K. (2001). Ozonation of soluble organics in aqueous solutions using microbubbles. *Ozone Science and Engineering, 23*(1), 77-87.

Wang, F., Smith, D.W., & El-Din, M.G. (2003). Application of advanced oxidation methods for landfill leachate treatment-A review. *Journal of Environmental Engineering and Science, 2*(6), 413-427.

Wang, K., Guo, J., Yang, M., Junji, H., & Deng, R. (2009). Decomposition of two haloacetic acids in water using UV radiation, ozone and advanced oxidation processes. *J Hazard Mater, 162*(2), 1243-1248.

Wang, N., Chelme-Ayala, P., Perez-Estrada, L., Garcia-Garcia, E., Pun, J., Martin, J.W., Belosevic, M., & Gamal El-Din, M. (2013). Impact of ozonation on naphthenic acids speciation and toxicity of oil sands process-affected water to Vibrio fischeri and mammalian immune system. *Environ Sci Technol, 47*(12), 6518-6526.

Wang, Z., Wang, X., Li, S., Xu, Y., Zhang, J., & Lv, F. (2008). Experimental Study on Downhole Gas Liquid Separation and Produced-Water Reinjection. Conference proceedings, SPE Annual Technical Conference and Exhibition.

Wells, P.G., Lee, K., & Blaise, C. (1997). *Microscale testing in aquatic toxicology: advances, techniques, and practice*: CRC Press.

Wolkers, H., Van Bavel, B., Derocher, A.E., Wiig, Ø., Kovacs, K.M., Lydersen, C., & Lindström, G. (2004). Congener-specific accumulation and food chain transfer of polybrominated diphenyl ethers in two Arctic food chains. *Environ Sci Technol, 38*(6), 1667-1674.

Wu, C., Gao, Z., Zhou, Y., Liu, M., Song, J., & Yu, Y. (2015). Treatment of secondary effluent from a petrochemical wastewater treatment plant by ozonation -

biological aerated filter. *Journal of Chemical Technology and Biotechnology, 90*(3), 543-549.

Wu, H., Lye, L.M., & Chen, B. (2012). A design of experiment aided sensitivity analysis and parameterization for hydrological modeling. *Canadian Journal of Civil Engineering, 39*(4), 460-472.

Wu, Y., Xia, L., Chen, R., & Hu, B. (2008). Headspace single drop microextraction combined with HPLC for the determination of trace polycyclic aromatic hydrocarbons in environmental samples. *Talanta, 74*(4), 470-477.

Wu, Y., Xia, L., Chen, R., & Hu, B. (2008). Headspace single drop microextraction combined with HPLC for the determination of trace polycyclic aromatic hydrocarbons in environmental samples. *Talanta, 74*(4), 470-477.

Xu, P., Drewes, J.E., & Heil, D. (2008). Beneficial use of co-produced water through membrane treatment: technical-economic assessment. *Desalination, 225*(1), 139-155.

Xu, P., Zeng, G.M., Huang, D.L., Feng, C.L., Hu, S., Zhao, M.H., Lai, C., Wei, Z., *et al.* (2012). Use of iron oxide nanomaterials in wastewater treatment: a review. *Science of the total environment, 424*, 1-10.

Yakimov, M.M., Timmis, K.N., & Golyshin, P.N. (2007). Obligate oil-degrading marine bacteria. *Current opinion in biotechnology, 18*(3), 257-266.

Yan, J., Wang, L., Fu, P.P., & Yu, H. (2004). Photomutagenicity of 16 polycyclic aromatic hydrocarbons from the US EPA priority pollutant list. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis, 557*(1), 99-108.

Yao, K.-M., Habibian, M.T., & O'Melia, C.R. (1971). Water and waste water filtration. Concepts and applications. *Environ Sci Technol, 5*(11), 1105-1112.

Yeung, C.W., Lee, K., & Greer, C.W. (2011). Microbial community characterization of produced water from the Hibernia oil production platform *Produced Water* (pp. 345-352): Springer.

Yiantzi, E., Psillakis, E., Tyrovola, K., & Kalogerakis, N. (2010). Vortex-assisted liquid-liquid microextraction of octylphenol, nonylphenol and bisphenol-A. *Talanta, 80*(5), 2057-2062.

Zacharis, C.K., Christophoridis, C., & Fytianos, K. (2012). Vortex-assisted liquid-liquid microextraction combined with gas chromatography-mass spectrometry for the determination of organophosphate pesticides in environmental water samples and wines. *J Sep Sci, 35*(18), 2422-2429.

Zhang, Y., Jiang, M., Zhao, L., & Li, F. (2009). Design and experimental study of hydrocyclone in series and in bridge of downhole oil/water separation system. Conference proceedings, ASME 2009 28th International Conference on Ocean, Offshore and Arctic Engineering.

Zhou, H., & Smith, D.W. (2002). Advanced technologies in water and wastewater treatment. *Journal of Environmental Engineering and Science, 1*(4), 247-264.

Zuijdgeest, A., & Huettel, M. (2012). Dispersants as used in response to the MC252-spill lead to higher mobility of polycyclic aromatic hydrocarbons in oil-contaminated Gulf of Mexico sand. *PloS one, 7*(11), e50549.